AFWAL-TR-84-2096
Volume I

ASPECTS OF HIGH-RESOLUTION GAS CHROMATOGRAPHY AS APPLIED TO THE ANALYSIS OF HYDROCARBON FUELS AND OTHER COMPLEX ORGANIC MIXTURES

Volume I - Chromatographic System Details

Wayne A. Rubey
University of Dayton
Research Institute
Environmental Sciences Group
Dayton, Ohio 45469

February 1985

Final Report for Period January 1980 - September 1980

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6563

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Paul C. Hayes

PAUL C. HAYES, JR.
Project Scientist, Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory

Arthur V. Churchill

ARTHUR V. CHURCHILL, Chief
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory

FOR THE COMMANDER

Benito P. Botteri

BENITO P. BOTTERI, Assistant Chief
Fuels and Lubrication Division
Aero Propulsion Laboratory

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/POSF *, W-PAFB, OH 45433 to help us maintain a current mailing list".*

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UDR-TR-82-156	5. MONITORING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-84-2096 Vol. I
6a. NAME OF PERFORMING ORGANIZATION University of Dayton Research Institute 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Aero Propulsion Laboratory (AFWAL/POSF) Air Force Wright Aeronautical Laboratories
6c. ADDRESS (City, State and ZIP Code) 300 College Park Dayton, Ohio 45469	7b. ADDRESS (City, State and ZIP Code) Wright-Patterson Air Force Base, Ohio 45433-6563
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Aero Propulsion Laboratory 8b. OFFICE SYMBOL (If applicable) AFWAL/POSF	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F-33615-77-C-2004
8c. ADDRESS (City, State and ZIP Code) Air Force Wright Aeronautical Laboratories Wright-Patterson Air Force Base, Ohio	10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO. 62203F; PROJECT NO. 3048; TASK NO. 05; WORK UNIT NO. 91
11. TITLE (Include Security Classification) ASPECTS OF HIGH-RESOLUTION GAS CHROMATOGRAPHY	
12. PERSONAL AUTHOR(S) Wayne. A. Rubey	
13a. TYPE OF REPORT FINAL 13b. TIME COVERED FROM Jan. 80 TO Sep.80	14. DATE OF REPORT (Yr., Mo., Day) 85 Feb. 4 15. PAGE COUNT 213
16. SUPPLEMENTARY NOTATION Report prepared under Senior Investigator Program, Task #40	

17. COSATI CODES		
FIELD	GROUP	SUB. GR.
07	01	03
21	04	05

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
High-resolution gas chromatography (HRGC); shale oil; fused silica capillary columns; open tubular capillary (OTC); multidimensional gas chromatography; elution zone;

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Turbine engine fuels are complex mixtures of hydrocarbons which have until recently, been obtained almost exclusively from petroleum. There is growing interest in developing alternative feedstocks for the eventual production of high-quality turbine engine fuels. The major analytical technique for separating the chemical constituents and analyzing fuels and synfuel feedstocks is high-resolution gas chromatography (HRGC), and the extreme chemical complexity of these hydrocarbon mixtures continues to challenge even the most sophisticated HRGC techniques. Therefore, the principal objective of this research was to identify and evaluate advanced HRGC instrumental procedures which show potential for improving the analysis of hydrocarbon jet fuels and various feedstocks.

A gas chromatograph can be viewed as an assembly of individual components arranged to form a time invariant linear system. Accordingly, a systems approach has been used in this investigation to study, refine, and modify HRGC instrumentation. The chromatographic

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL P.C. Hayes, Jr.	22b. TELEPHONE NUMBER (Include Area Code) (513) 255-3190 22c. OFFICE SYMBOL AFWAL/POSF

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

11. AS APPLIED TO THE ANALYSIS OF HYDROCARBON FUELS AND OTHER COMPLEX ORGANIC MIXTURES, Volume I, Chromatographic System Details.

19. analysis of a complex organic mixture requires a system capable of efficient quantitative transport of solute molecules admitted to the system, and the injection of a complex broad-molecular-weight-range organic sample presents special problems to HRGC analysis. An important topic relevant to complex organic mixture analysis and the generation of analytical data (qualitative and quantitative) is elution zone profile. The complete HRGC system must be capable of migrating, sensing, and eventually recording symmetrical zone profiles accurately. For maximum information content to be obtained from an HRGC system, the output signal must be properly amplified and recorded. Also, the many devices that handle and display the output chromatographic signal are especially important with respect to quality of the analytical information.

In the future, aviation turbine fuels, along with geochemical and biomass feedstocks, will continue to be analyzed by HRGC, since research in this field and in this technique is quite active.

Originator Supplied Keywords Included

See DD1473

FOREWORD

This report was prepared by the Environmental Sciences Group within the Research Institute of the University of Dayton, Dayton, Ohio 45469. The work reported herein was conducted under Task 40 of the Senior Investigator Program on Contract F33615-77-C-2004, which was funded by the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433-6563. The Project Officer for this effort was Major Donald D. Potter (AFWAL/POSF). This document is Volume I of the two-volume report and the experimental portion of this work was conducted between January and September of 1980, while the literature review encompassed 1983.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the support and encouragement of the Air Force Project Officer, Major Donald D. Potter, of the Aero Propulsion Laboratory (APL). The author is also indebted to several other APL personnel for their help during the course of this investigation. The chromatography consultations with Paul C. Hayes, Jr. and Edward W. Pitzer were of continual value with respect to assessing the operation of the in-house laboratory analytical instrumentation. The sample insertion experiments performed by Charlotte R. Eigel clarified many of the variables and other aspects associated with the split sample injection process. Also, the exchanges with Ronald D. Butler relative to high-resolution gas chromatography theory and applications were of considerable help during the course of this investigation.

Within the Research Institute at the University of Dayton, several of my colleagues were especially helpful. The laboratory work of William E. Dirkes, Jr. was of key importance during the early high-resolution GC experiments. The mathematical portions of the appendices were reviewed by Jerry Strange. Anita Cochran has been especially helpful in correcting my many grammar errors and has improved the readability of the report. In the early part of this work, Don S. Duvall encouraged the undertaking of this research and it was completed under the administrative leadership of our present Group Leader, Barry Dellinger. And finally, the author is especially grateful to our secretary, Julia L. Cochran, for the diligent typing of the various text drafts.

TABLE OF CONTENTS

FIGURES

TABLES

SECTION I

INTRODUCTION

Turbine engine fuels are complex hydrocarbon mixtures normally derived from organic feedstocks such as petroleum. Typical jet fuels are extremely complicated, as they contain between 10^2 and 10^4 different chemical compounds. Although such a fuel may consist primarily of normal paraffins, branched paraffins, and aromatic hydrocarbon compounds, it will also contain small quantities of organic substances that fall into several chemical classes. Many of these low-concentration compounds can have a profound effect on certain properties of a fuel. In view of this extreme chemical complexity, the thorough chemical characterization of such hydrocarbon mixtures requires highly sophisticated analytical capabilities.

Recently, concern has increased for the development of alternate hydrocarbon energy sources to serve as basic feedstocks for the eventual production of high-quality turbine engine fuels. Oil shale deposits represent some of the most promising hydrocarbon sources in the United States, and there is considerable interest in developing full-scale processes for generating abundant quantities of shale oil. Eventually jet fuels derived from shale oil must be comparable and compatible with jet fuels obtained from petroleum-based feedstocks.

High-resolution gas chromatography (HRGC) is the major analytical technique for separating and analyzing complex mixtures of volatile hydrocarbons. Although gas chromatography was introduced commercially in the middle 1950's, this basic analytical technique is currently experiencing expanded application, particularly with respect to separating complex organic mixtures. In the past few years, HRGC has been used to achieve enhanced analytical separations and to obtain more descriptive analyses of various organic mixtures.

The chemical complexity of a turbine engine fuel continues to challenge even the most sophisticated of the present HRGC techniques. However, advances are continually being made in this technology, and a variety of procedures are being researched for improving the various chromatographic characterization methods as applied to the detailed analysis of jet fuels.

SECTION II

RESEARCH OBJECTIVES

The primary objectives of this research are to identify and evaluate advanced high-resolution gas chromatographic (HRGC) instrumental procedures which show potential for improving the analysis of hydrocarbon jet fuels and various feedstocks. This research concentrated on the following essential objectives:

1. Evaluate the performance of commercial high-resolution gas chromatography instrumentation presently used in the Fuels Branch of the Fuels and Lubrication Division of the Aero Propulsion Laboratory at the Air Force Wright Aeronautical Laboratories, located at Wright-Patterson Air Force Base. Recommend chromatographic components, equipment, or procedural modifications which will permit continual expansion of these analytical capabilities.

2. After evaluating the range of analytical requirements, recommend, specify, or fabricate a series of open tubular gas chromatographic separation columns that would be most applicable for chromatographically analyzing hydrocarbon fuels and associated shale oil products. Consider the application of special-purpose HRGC columns for conducting trace analyses with certain types of fuels.

3. Identify and quantitatively evaluate the various sources which contribute to chromatographic output zone profile asymmetry, commonly referred to as elution peak tailing. After characterizing the various potential sources, recommend procedures for appropriately installing open tubular gas chromatographic (GC) columns in GC

instruments. Such optimized installations should minimize asymmetric elution behavior and other chromatographic output signal distortions in conventional column arrangements and in special column installations such as capillary effluent splitters.

4. Investigate the various sample injection procedures currently used for injecting undiluted complex samples into capillary columns. Determine the best available automated technique for injecting hydrocarbon fuels into high-resolution GC columns. Determine the parameters which affect the linearity of split reproducibility of this particular injection technique. Assess possible modifications to improve sample injection performance.

5. Evaluate the application of the Kovats retention index system to the various gas chromatographic operational modes, such as isothermal gas chromatography (ITGC), programmed temperature gas chromatography (PTGC), and variations thereof. Through the use of time normalization procedures, recommend appropriate GC conditions for obtaining the greatest amount of analytical GC data in a given time for highly complex samples.

6. Study the potential benefits of multidimensional gas chromatographic techniques for analysis of complex hydrocarbon mixtures. Identify the design and operational features which should be included in an instrumentation assembly that would be dedicated to the multidimensional gas chromatographic analysis of jet fuels.

SECTION III

BACKGROUND

1. JET FUELS

For the past several decades, practically all aviation turbine fuels have been obtained from petroleum-based feedstocks. These jet fuels, produced in very large quantities at petroleum refineries, have consisted essentially of complex mixtures of petroleum-derived hydrocarbons.

The physical and chemical properties of jet fuels have frequently been described in military specifications (e.g., MIL-T-5624 [1] and its revision). Typically, petroleum based jet fuels have had to meet requirements relative to distillation, density, surface tension, viscosity, resistance to formation of gum deposits, and limitations with respect to sulfur content, particulate matter, and acidity. These fuels have also had to conform to vapor pressure, heat of combustion, flame luminescence, thermal stability, freezepoint, flashpoint, and smoke point criteria. In addition, these various jet fuels have been required to meet specification requirements relative to filtration time, the ability to separate water out of the fuel, and chemical requirements with respect to aromatic and olefinic content. Recently, there has been increased interest in combustion and the possible formation of pollutants in jet engine exhaust [2,3]. Accordingly, basic studies are being conducted on the formation of soot and polycylic aromatic hydrocarbons during combustion of gas turbine fuels.

2. SHALE OIL AND SYNFUELS

In the 1970's, increased attention was directed toward obtaining hydrocarbon fuels from nonpetroleum feedstocks [4], specifically, interest focused on obtaining acceptable fuels from coal, oil shale deposits, tar sands, and various forms of biomass. Indeed, the cumulative energy stored in these various synthetic

fuel (synfuel) sources is enormous. Fortunately, the United States has very large deposits of coal and oil shale.

The feasibility of producing jet fuels from shale oil has already been demonstrated [5,6]. This particular synfuel source is promising [7,8] as many processes are being developed for extracting hydrocarbons from our vast oil shale deposits, such as those in the Green River formation in Colorado, Utah, and Wyoming. It has been estimated that these particular deposits could yield over 600 billion barrels of shale oil. Other large oil shale deposits in the United States and in Europe are also seen as future sources of energy and hydrocarbon feedstocks.

Different shale oil materials are now being analyzed and characterized. The U.S. National Bureau of Standards now provides a standard reference sample of shale oil, thus permitting development of analytical procedures which can be readily evaluated, tested, and compared in different laboratories.

3. THE ROLE OF CHROMATOGRAPHY

Chromatography plays a major role in fuel characterization. Chromatographic techniques were applied in the latter 1950's for characterizing gasolines, kerosines, and the various jet fuels of that day. However, there has been a tremendous increase in the analytical capability of the various chromatographic techniques. Today, both gas chromatography and liquid chromatography are used to characterize petroleum feedstocks, shale oils [9], kerosines, gasolines, and jet fuels. Even so, it is fair to say that the extreme chemical complexity of these hydrocarbon mixtures still requires greater chromatographic separation than is possible by existing high-resolution chromatographic techniques. Thus, chromatography is a very active area of instrumental analysis research, advances are being made, and the future is promising for obtaining highly sophisticated analyses of these organic mixtures.

In efforts directed at reducing sample complexity, high-performance liquid chromatography (HPLC) is frequently used to separate the very complex organic mixtures into families of compounds [10,11], thereby simplifying the eventual analysis of the various classified fractions [12].

High-resolution gas chromatography (HRGC) is the major tool for obtaining the separation and chromatographic characterization of the individual compounds in these chemical mixtures. HRGC, with its application to the analysis of jet fuels and various shale oil samples, is the subject of this research report.

SECTION IV

APPROACH TO HIGH-RESOLUTION GAS CHROMATOGRAPHIC INSTRUMENTATION SYSTEMS

A gas chromatograph can be viewed as an assembly of individual components arranged to form a casual, time-invariant, linear system [13]. Therefore, a systems approach is used in this investigation to study, design, and modify high-resolution gas chromatography (HRGC) instrumentation. It is especially beneficial that a gas chromatograph can be represented as a linear system, since this permits the detailed characterization of chromatographic zone migration.

1. SYMMETRICAL ELUTION PROFILES

The chromatographic analysis of a complex organic mixture requires a system capable of efficient quantitative transport of the various solute molecules admitted to the system. Such instrumentation must be capable of efficiently migrating the various solutes, and it must permit the accompanying zone dispersion of the migrating species to be strictly random in nature.

A concentration zone of like molecules emerging from a gas chromatograph should theoretically be distributed in time as described in Figure 1. This concentration versus time profile is known as a Gaussian density distribution (see Abbreviations and Symbols for term designations). The unbiased migration of like species through a long chromatographic column will indeed correspond very closely to this Gaussian profile.

In HRGC, it is very important that the chromatographic system be capable of generating symmetrical Gaussian elution profiles. As can be seen in Figure 2, the crest region of the solute zone is important to establishing the identity of the emerging solutes. The leading and lagging regions at the base of the profiles are also of key importance to establishing the baseline, i.e., the analytical zero reference level. This baseline permits both peak height and integrated zone profile

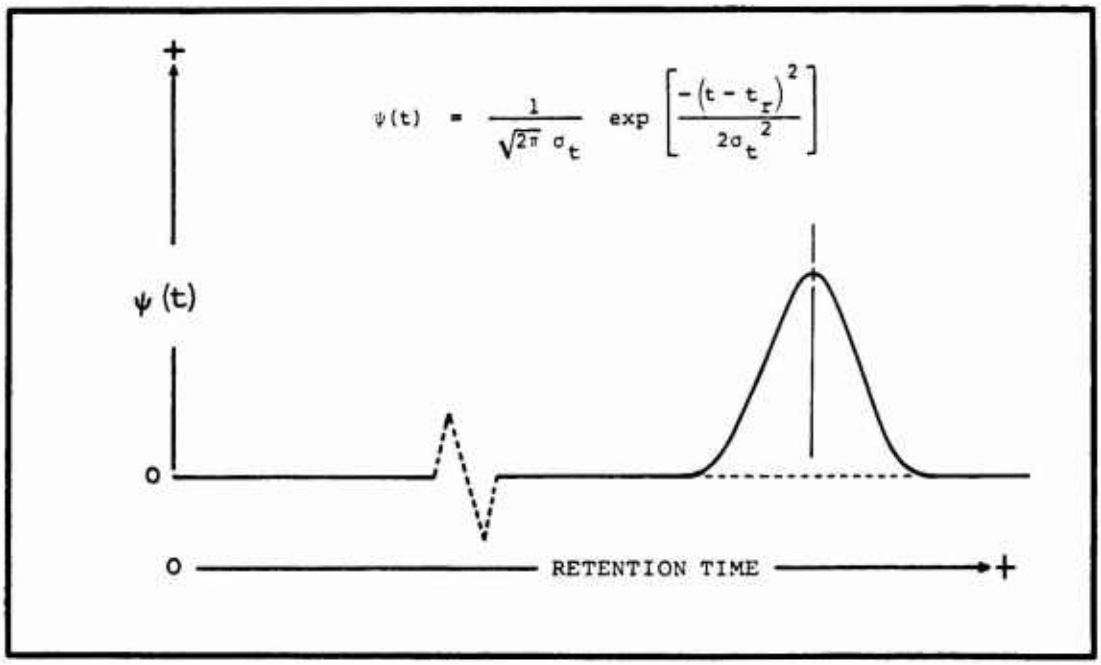


Figure 1. Gaussian gas chromatographic elution zone.

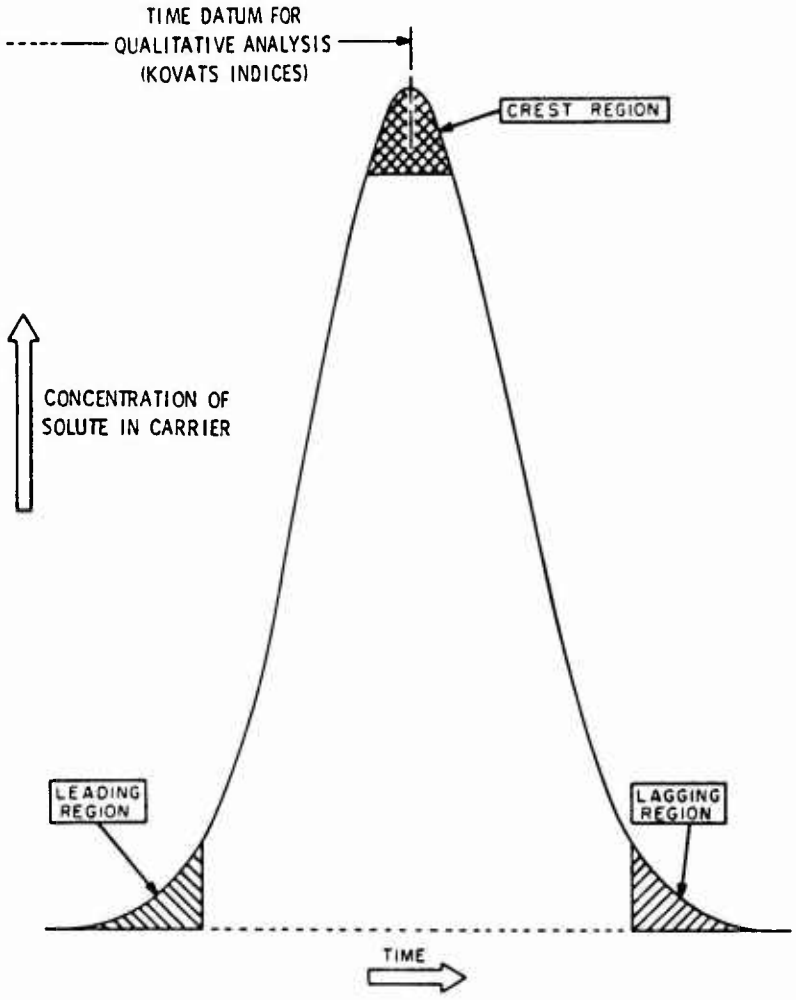


Figure 2. Symmetric elution zone profile.

data to be obtained, thereby establishing the basis for the quantitative determination of the species in question.

If the chromatographic system generates profiles that depart significantly from the Gaussian profile, significant errors can be introduced into both the qualitative analysis and the gas chromatographic quantitation. (This topic will be dealt with at length in Sections VI and VII. Also, Appendices A and B address, in part, this same topic.)

In the HRGC of the future, it will be of paramount importance that each pertinent component of the entire chromatographic system be designed for delivering symmetrical elution profiles. Schomberg, in his recent review of open tubular column (OTC) gas chromatography [14], stated that improving elution peak tailing behavior in HRGC columns is more important than increasing separation efficiency. This is valid; unless the chromatographic system is capable of generating symmetrical profiles, a mere increase in chromatographic efficiency is superfluous. In short, the gains from increasing the number of theoretical plates can be easily lost due to elution profile asymmetry or assorted forms of exponential peak tailing.

The first objective in chromatographic analysis is to obtain chromatographic separation of the chemical constituents. In other words, one must adequately disengage the solute zones. Once two adjacent solute zones have been sufficiently disengaged, they can be quantitatively measured. If their time of elution relative to standard substances is known, a certain measure of qualitative interpretation can be applied.

Figure 3 shows the partial disengagement of two chromatographic zones, one containing compound i and the other containing compound j. As seen in this illustration, these are two partially separated zones of Gaussian profile. The primary chromatographic objective is to obtain sufficient resolution [15,16] between these two characteristic zones so that the subsequent analysis can be accurate [17].

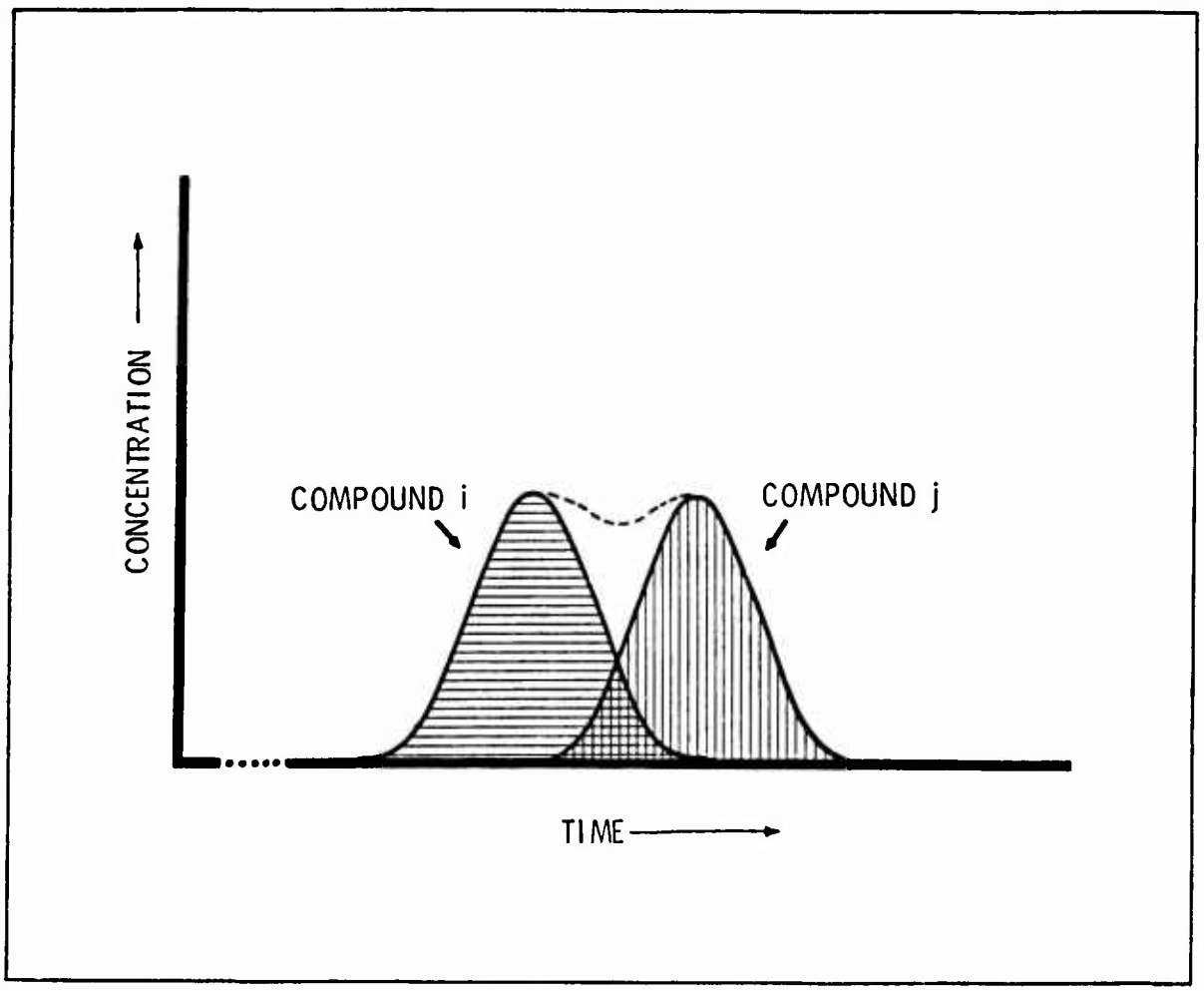


Figure 3. Partially disengaged solute zones.

2. SYSTEMS APPROACH

In a continuous process such as chromatography, the HRGC instrument can be viewed as a series of instrumental stations. Figure 4a shows that study and characterization of the sequential transport behavior can take place as the sample passes through the series of stations. This basic systems approach [18] has been applied to other studies [19-21] where a gas chromatograph has been the central member in extended instrumentation systems. Figure 4(b) is a single block diagram depicting such systems. This approach permits one to view HRGC instrumentation as a series of components or operational processes arranged sequentially as shown in Figure 4(c), which exemplifies the systems approach to chromatography addressed in this report.

In the various basic forms of column chromatography, the major component in the instrumentation assembly is the separation column. Accordingly, the behavior of chromatographic separation columns has been studied a great deal. Even so, in many cases the excellent behavior of a high-quality chromatographic column can be seriously compromised if the column is not properly positioned in the chromatographic instrument. This situation is especially common in the field of HRGC where many precolumn and postcolumn sources of distortion can seriously affect the eventual chromatographic output performance.* These potential distortion sources must be studied and thoroughly characterized to obtain the ultimate performance from the chromatographic instrumentation. Here again, the systems approach is of considerable value in diagnosing and evaluating these possible distortion sources.

---

*Throughout this discussion, we make the assumption that a migrating solute zone experiences no thermolysis, chemical reactions, or various other types of chemical degradation during the course of its traverse through the HRGC flowpath. Also, spurious elution profiles have been observed as a result of decomposition or oxidation of the stationary phase, particularly at the inlet region where sample residues can catalyze decomposition. Both of these types of observed behaviors are unacceptable chromatographic procedures as they violate quantitative transport criteria.

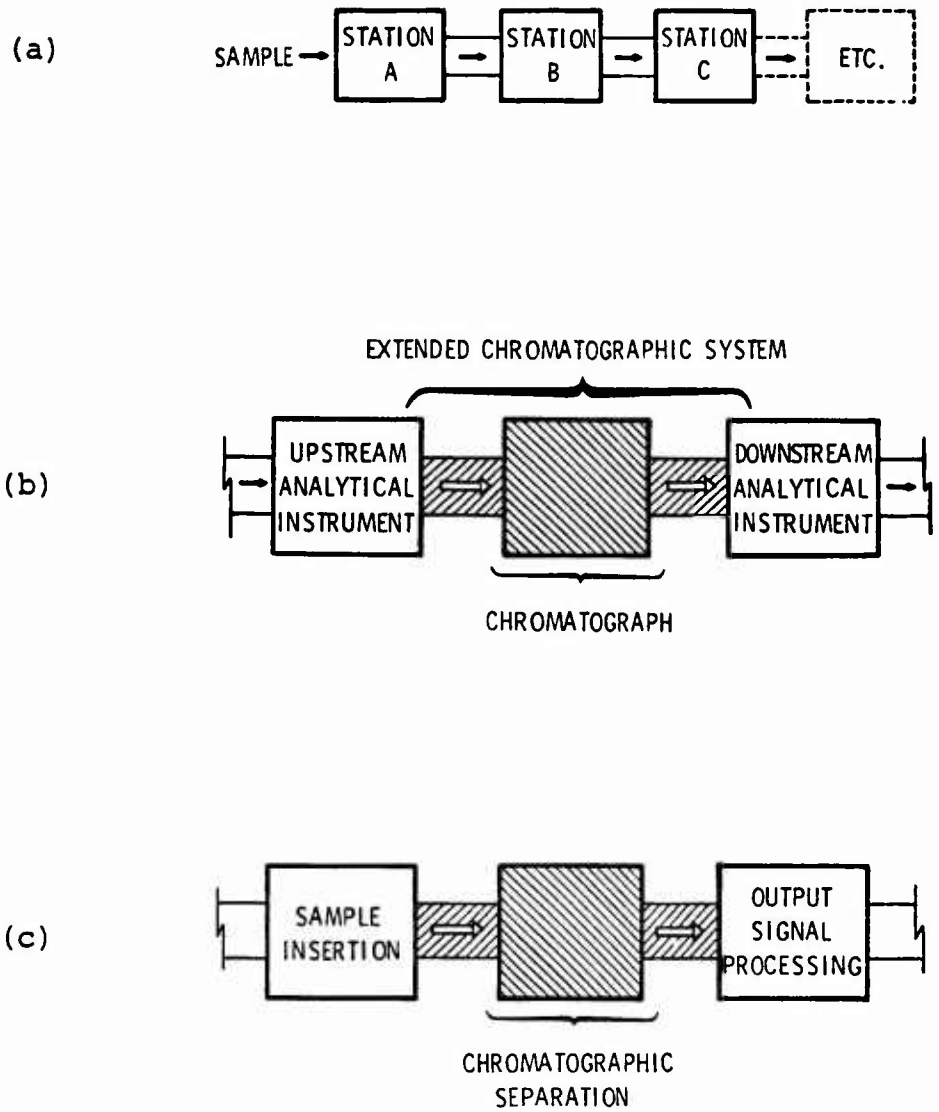


Figure 4. Block diagram of basic systems approach.

Figure 5 shows three general forms of zone profiles which can be intentionally or inadvertently generated in gas chromatography. These three types of profiles (i.e., R, G, and E) can be individually generated in precolumn components, in chromatographic separation columns, and in various postcolumn components and instrumentation (see Figure 6). The number of possible combinations, permutations, or arrangements into which these three different profiles can be expressed is worth investigating. Accordingly, a permutation of n things taken r at a time with repetitions is an arrangement obtained by putting any member of the set in the first position, any member of the set, including a repetition of the one just used, in the second, and continuing this until there are r positions filled. The total number of such permutations or arrangements is

$$P_A = n^r \ .$$

Consequently, for the three profiles shown in Figure 5, it is possible to obtain 27 different combinations for a basic gas chromatographic system. Fortunately, the elution zone contour that results from combinations of these three basic profiles (and other possible distributions) can be expressed mathematically. This topic is discussed further in Section VI and in the Appendices to this report.

In the early days of gas chromatography, when the analyst wanted to accomplish a certain difficult chromatographic separation, one option was to change the chromatographic stationary phase employed in his instrument. However, with HRGC, the arsenal of separation columns containing a large assortment of stationary phases is not needed. Six well-chosen chemically bonded stationary phases (see Table 1) would probably be suitable for the vast majority of separations encountered in the HRGC laboratory [22].

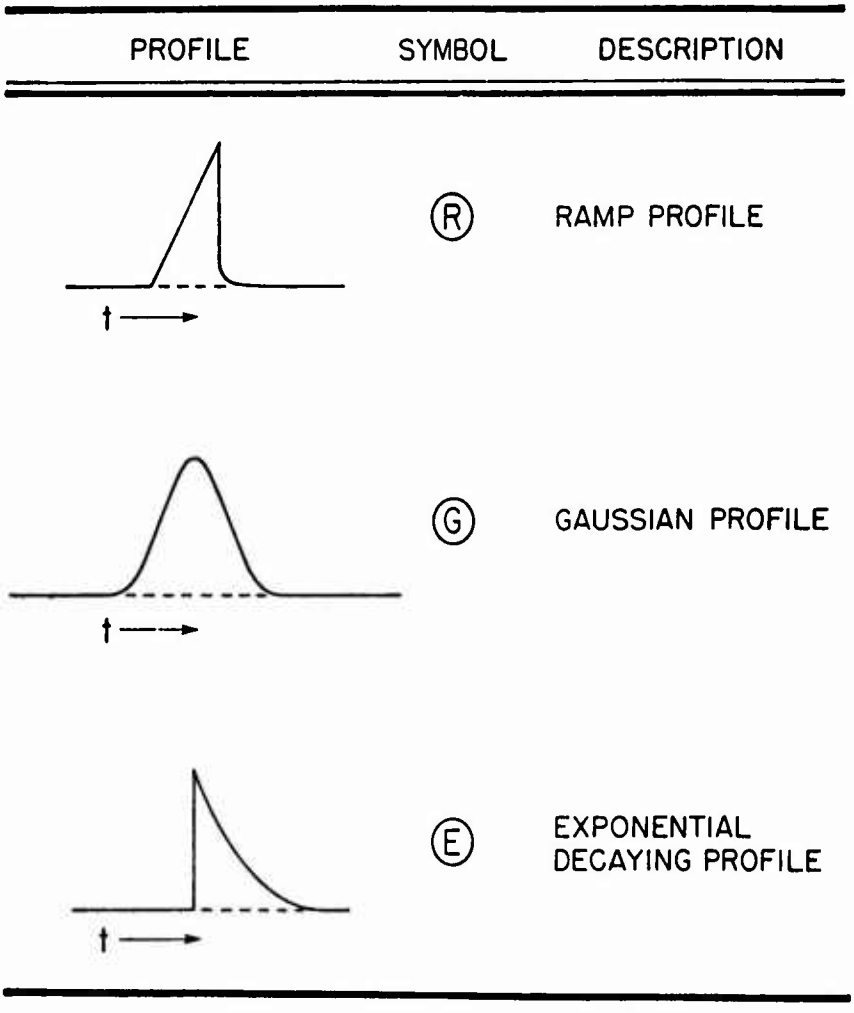


Figure 5. Three general forms of chromatographic zone profiles.

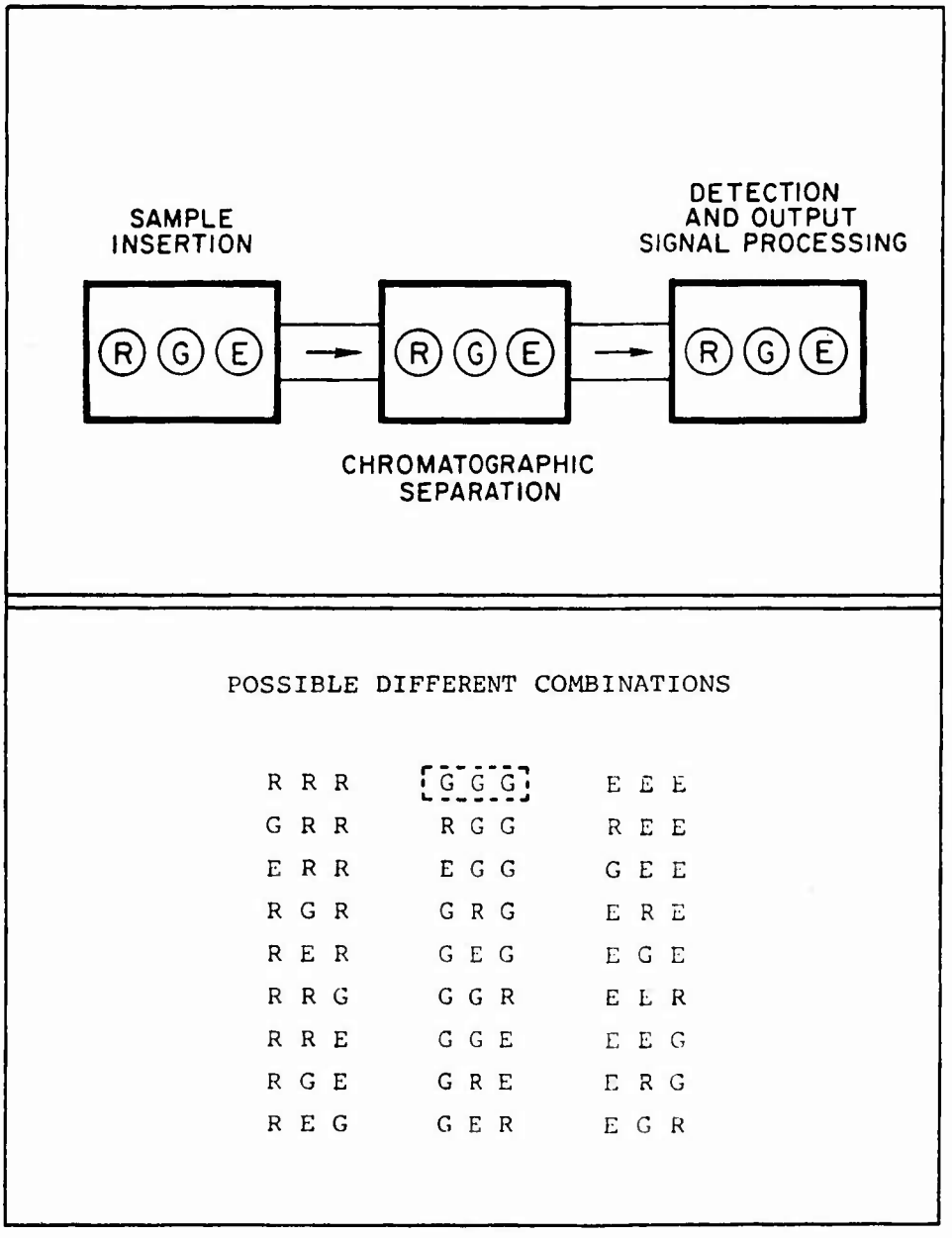


Figure 6. Different combinations of solute zone profiles.

TABLE 1

ASSORTMENT OF SELECTIVE STATIONARY PHASES

Description	Polarity
Dimethyl silicone	non-polar
5% phenyl methyl silicone*	slightly polar
50% phenyl methyl silicone	moderately polar
Polyethylene glycol	polar
Cyanopropyl silicone	moderately polar**
Trifluoropropyl methyl silicone	moderately polar**

*High temperature phase that is a substitute for the diethylene glycol succinate phase from earlier listing [22].

**Special functional group phase.

The capabilities of HRGC have also been enhanced by recent advances in high-performance liquid chromatography (HPLC). This technique can be used to obtain preseparations or as a process by which a very complex hydrocarbon mixture can be fractionated and classified according to families of chemical compounds prior to injection into a HRGC instrument. In short, this is a process for simplifying the subsequent high-resolution chromatographic separations.

JP-4 jet fuel has an initial boiling point of approximately 20°C, and the heaviest species in this hydrocarbon fuel will probably boil at temperatures somewhat less than 300°C. A typical JP-4 fuel may contain carbon numbers ranging from C_4 to C_{16}. However, an unfractionated shale oil may contain carbon numbers ranging from C_4 to C_{34}. For samples with such a broad range of constituent volatilities, the GC technique of programmed temperature gas chromatography (PTGC) is imperative. This technique has received considerable attention relative to separating organic mixtures which possess a wide range of molecular weights, and it has unique and beneficial operational aspects. For example, it is able to thermally focus the injected sample into a short segment of the column and then to differentially migrate the sample through the long gas chromatographic flowpath. This thermal focusing feature and several associated aspects are especially beneficial to instrumental analysis systems. More benefits of PTGC are discussed in Volume II of this report.

SECTION V

BRIEF DISCUSSION OF SAMPLE INSERTION

The injection of a highly complex and broad-molecular-weight-range organic sample, e.g., jet fuel, shale oil, crude oil, etc., presents special problems with respect to high-resolution gas chromatographic (HRGC) analysis. This type of organic mixture should not be placed in a solvent and then subjected to analysis, since any solvent (along with its impurities) would interfere and seriously mask sample constituents. In short, to obtain maximum analytical information, the chromatographic analysis of an unfractionated complex hydrocarbon fuel should be conducted in its undiluted form, although this requirement places special demands upon present HRGC instrumentation.

At present, the largest sample that a typical OTC can accept without overloading is approximately 0.01 microliters of liquid, and this would apply only for a very complex wide-boiling-range sample which contains few prevailing constituents. There are at present no liquid microliter syringes that can repetitively deliver such a small quantity of liquid to the head of a column with accuracy and without fractionation of the sample. The need for analyzing vast quantities of jet fuel samples necessitates the use of automatic sample injection techniques, and as these samples have such a wide range of volatile constitutents, special demands are placed upon the sample insertion process. High-performance sample insertion procedures are definitely needed. Today, it is the sample insertion process which effectively limits the quality of the analysis of a complex hydrocarbon fuel by HRGC.

Sample insertion techniques are needed which would not produce degradation of thermally sensitive sample constituents. Thus, it appears that a sampling insertion process is needed which would not subject the sample to an excessively high temperature at the chromatograph inlet. A sample inlet assembly is needed which eliminates sample "carry-over" from previously

injected samples. Also, a suitable inlet assembly for such complex mixtures must not contaminate an admitted sample with impurities such as septum bleed, organic leachate from upstream system components, compounds arising from the decomposition of polymeric ferrules, etc.

Four sample insertion techniques are now widely used in HRGC: (a) the split mode of injection, (b) the splitless injection technique, (c) the direct injection procedure, and (d) the on-column sample insertion process. None of these in its presently available form is completely acceptable for conducting numerous repetitive analyses with jet fuel samples.

As stated earlier, sample insertion is presently the weakest link in HRGC as applied to the analysis of complex hydrocarbon mixtures. This situation has been recognized, and recently Schomburg presented an excellent paper [23] covering the present sampling systems in OTC gas chromatography and reviewing the current state of the technology with respect to recent injection procedures. The importance of addressing the sample insertion aspects of HRGC was also highlighted recently by a special international symposium [24] at which the only topic was injection techniques in capillary gas chromatography. Research into improving sample insertion procedures in HRGC is being conducted in many laboratories around the world, and indications are that new and improved procedures will be available soon.

Recognizing the extreme importance (and attendant problems) associated with the injection of a highly complex and broad-molecular-weight-range organic sample in HRGC, it was decided that this topic should be addressed separately. Thus, Volume II of this report, "Survey of Sample Insertion Techniques," discusses the present methods of sample insertion with OTCs. The variables and operation aspects associated with the various types of sample injection devices are also presented. In addition, some experimental data obtained with different injection techniques are

discussed. Volume II also presents systematically the features and limitations of injection inserts, OTC precolumns, and different types of microliter syringes.

SECTION VI

CHROMATOGRAPHIC SEPARATION

1. DESIGNS AND PROPERTIES OF SEPARATION COLUMNS

The accurate characterization of complex hydrocarbon fuels can presently be accomplished best by high-resolution gas chromatography. These chromatographic separations are performed almost exclusively with open tubular columns (OTCs) of considerable length. Research aimed at improving the performance of OTCs is making progress in the methods of separating complex organic mixtures.

Marcel Golay not only proposed and prepared the first gas chromatographic OTCs [25,26], but also postulated what ought to be the ideal HRGC column. Basically, he contended that an ideal separation column would have a long narrow bore and a velvet-like coated interior surface. Thus, such a long narrow flowpath would have a large, uniform surface area for containing a sizeable quantity of stationary phase which would still be distributed as a uniform thin film. Some progress has been made toward these types of columns, as whisker-walled open tubular columns have been produced and evaluated [27]. Golay also theorized [26] that there would be distinct advantages in a rectangular cross-section open tubular column. However, he has recently reconsidered the practical merits of noncircular cross-section OTCs [28,29] and now contends that circular cross-section flowpaths are superior.

HRGC columns have been made with a variety of tubing materials. Although metal and plastic tubing were used in the early evolution of HRGC technology, glass and fused silica are preferred for present OTCs. The bulk compositions of some of the common types of glasses used for making columns are shown in Table 2. Soft Glass and Pyrex have been used extensively as tubing materials for glass capillary columns. The recent introduction of flexible fused silica narrow-bore tubing [30] is a major step in OTC technology, because it is now possible to prepare efficient OTCs [30,31] with long-life capabilities.

TABLE 2

BULK COMPOSITION OF CERTAIN GLASSES

Glass Type	Composition of Glasses					
	SiO_2	Al_2O_3	Na_2O	CaO	MgO	B_2O_3
Soda Lime (R-6)	73	1	17	5	4	–
Borosilicate (Pyrex 7740)	81	2	4	–	–	13
Fused Silica	100	Less than 1ppm total metals				
R-6 (SO_2 treated) Surface to 100 Å	100	Less than 1ppm total metals				

Considerable chromatographic research [30,32] is being focused on glass surface chemistry. The objective of this surface characterization is to obtain glass tubing surfaces which: (a) have very low metal ion contents, (b) exhibit negligible catalytic effects at elevated temperatures, (c) possess extremely good inertness or freedom from adsorptivity, (d) can be easily wetted by a variety of stationary phases, and (e) present a surface conducive for attachment of chemically bonded stationary phases.

Several current techniques for drawing glass tubing permit the subsequent modification of the tubing interior with processes such as surface leaching, the forming of whiskers, etc. Consequently, a glass OTC could probably be constructed to almost any configuration [33], thereby permitting versatility in designing and fabricating special HRGC columns.

Several years ago, there was a definite preference for HRGC stationary phases with a fluid consistency. Recently, workers have preferred stationary phases of a higher molecular weight and a gum-like consistency. Gum phases tend to withstand solvent overloading better than the more fluid stationary phases. However, more important is the fact that gum phases can better tolerate rapid temperature changes without the thin liquid layer forming into surface pools or droplets. Fluid phase OTCs which receive extensive thermal cycling in the programmed temperature mode tend to form stationary phase droplets and bare spots* more readily than do gum phase columns.

Recent work [34,35] wherein stationary phases have been chemically bonded to the tubing wall surface, synthesized in situ, or cross-linked, shows considerable promise of very high-performance OTCs. A chemically bonded phase in a flexible fused

*Stationary phase droplets and microscopic areas of exposed tubing wall are considered sources of elution profile asymmetry and column inefficiency.

silica open tube represents a HRGC column of strong potential. Stationary phases of different polarity are now being chemically bonded [36] to the wall of various glass and fused silica tubes. As these phases are not extractable, they exhibit very low column bleed even at elevated temperatures, and the stationary phase pooling problem as discussed above is practically nonexistent with these chemically bonded phase OTCs. In addition, most of these fused silica OTCs can be flushed with solvents to remove contaminants lodged in the column interior. It is anticipated that these bonded stationary phases could also be applied to columns of differing internal configurations, such as whisker-walled tubes [37] and other types of chromatographic gas flowpaths.

Surface deactivation [38,39] is also receiving considerable attention in OTC technology. Fortunately, progress is being made with the use of several deactivating procedures for the various glass and fused silica tubings.

Probably the major physical advantage of a capillary column is its gas path openness, that is, its high permeability, which permits very long columns to be operated at reasonable instrument inlet pressures. As the total efficiency of a chromatographic column is directly proportional to its length, very high-efficiency gas chromatographic columns can be made via basic open tubular construction. The practicing chromatographer should be aware that, although chromatographic efficiency is directly proportional to column length, chromatographic resolution usually increases by the square root of column length [40]. It is still advantageous to use rather long OTCs for very difficult chromatographic separations, although the maximum concentrations of emerging peaks will be much smaller and analysis times will be longer. (See that portion of Appendix A which addresses the decline in a solute zone's maximum concentration during migration through OTCs.) Several researchers [41,42] routinely use OTCs of 300 meters and longer which can generate over 10^6 theoretical plates.

When a long chromatographic column is used, the gas flow and temperature parameters of the chromatographic system must be adjusted for maximum performance. For example, the carrier gas velocity must be carefully selected to produce maximum solute separation, and the rates of temperature programming must be correspondingly very low, usually in the region of 0.5° to 2.0°C min^{-1} for some of the longer OTCs. The maximum resolution for a pair of solute zones generally occurs at the lowest temperature which permits practical migration velocities. Therefore, it is counterproductive (from a resolution standpoint) to program the temperature of a long OTC at excessive rates, since that would cause the main migration of the solute to occur at higher temperatures, thereby reducing chromatographic resolution.

When a long OTC is being used, a convenient operational trade-off can usually be made. Specifically, in order that data be obtained in a shorter time, the carrier gas velocity can be increased to a higher-than-normal level so that the solutes are traversing the column rapidly. Thus, resolution is traded off for shorter analysis time.

Figure 7 shows a gas chromatographic tracing corresponding to a jet fuel generated with a relatively short capillary column. The carrier gas velocity here was much higher than optimum and the entire PTGC tracing was completed in eight minutes. Similar results could be obtained with a much longer column, where the carrier gas velocity would be even higher. The same jet fuel sample analyzed in Figure 7 was chromatographed with a longer column, and the corresponding chromatogram is presented in Figure 8. Other workers [43,44] have performed very rapid separations of high-molecular-weight materials by using hydrogen carrier gas at mean axial velocities of 0.5 to 1.5 meters per second. Thus, the use of hydrogen as the carrier gas is another option. A hydrogen carrier gas is definitely beneficial for rapid OTC separations and certain aspects of PTGC operation.

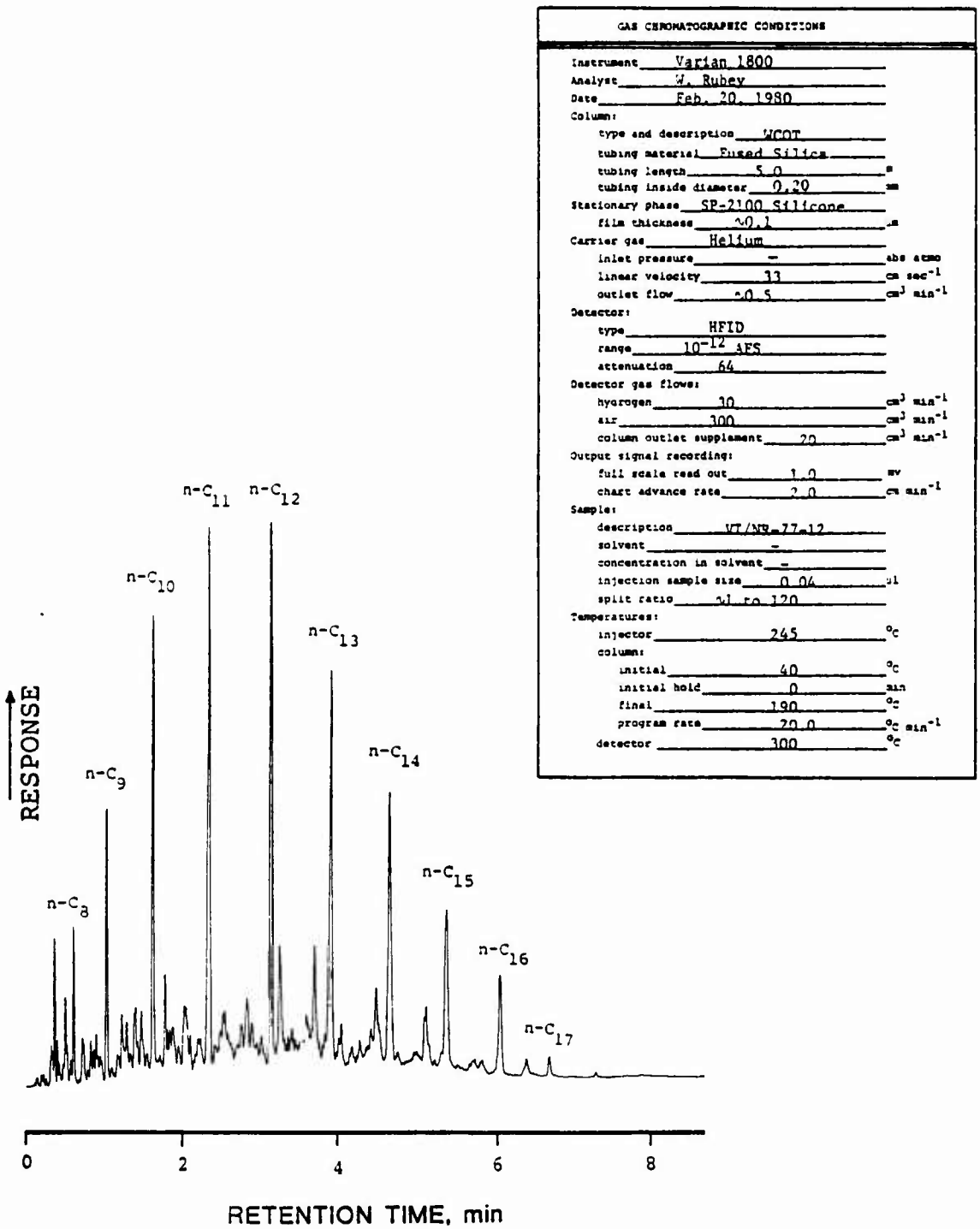


Figure 7. Rapidly generated chromatogram of a jet fuel.

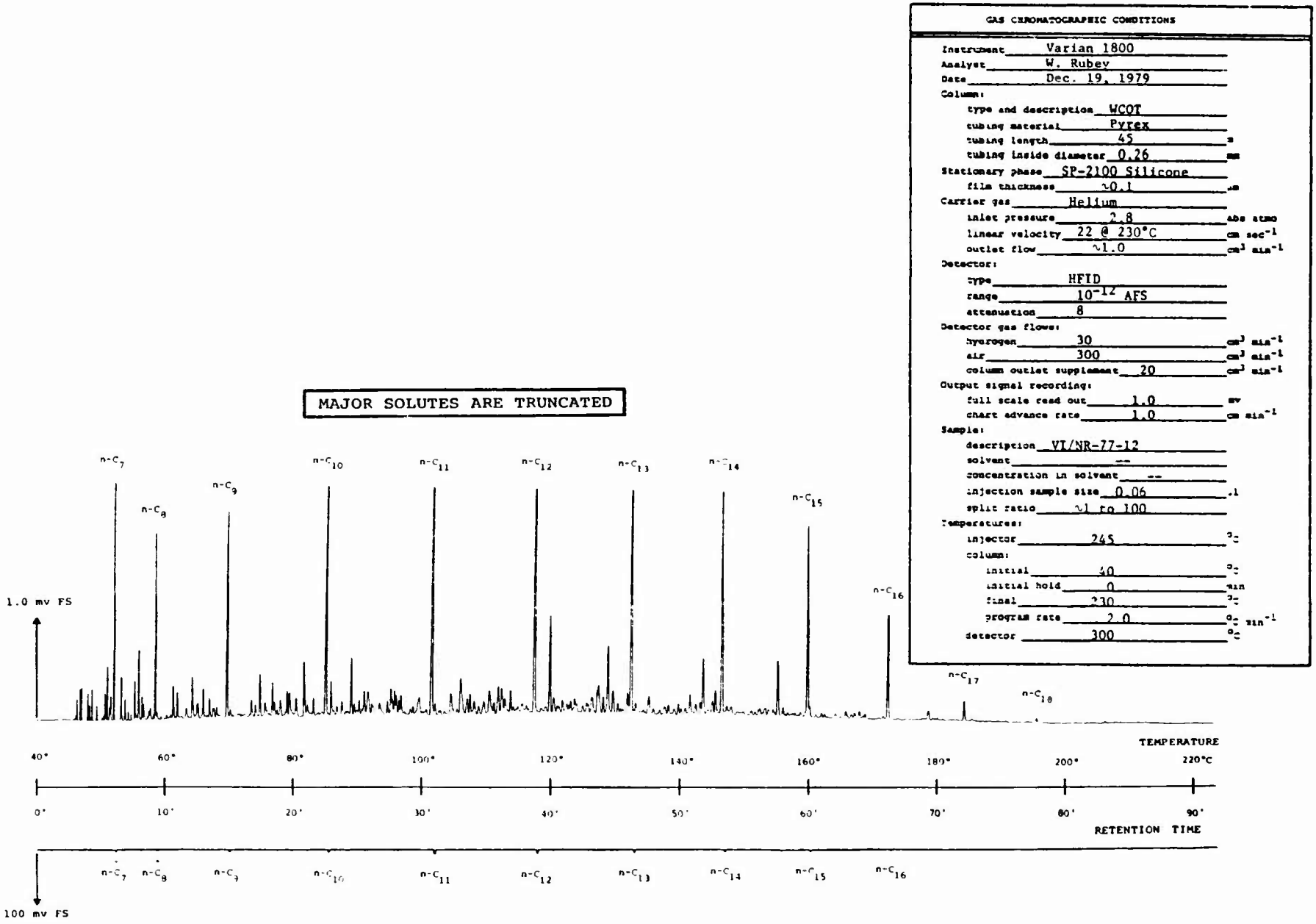


Figure 8. Chromatogram of a jet fuel obtained with a Pyrex glass open tubular column.

2. IMPORTANT OTC PARAMETERS AND OPERATING PROCEDURES

For the best possible performance from a HRGC column, the column parameters and the operating conditions must be optimized. Several available characteristics can be measured to evaluate the chromatographic efficiency of an OTC. Several criteria can be used for measuring the chromatographic resolution for a given pair of solvents; these are discussed in gas chromatography texts (e.g., see references 45 and 46). However, since the major concern in this work is obtaining adequate resolution for constituents in organic fuels (with the use of high "resolution" gas chromatography), the performance parameter that seems most applicable is resolution.

Chromatographic resolution can be stated in basic physico-chemical terms and can be graphically measured. Specifically, the extent to which a well-behaved pair of solute zones is chromatographically isolated is termed resolution and is expressed according to

$$R_{ij} = 2\left(\frac{t_{r,j} - t_{r,i}}{w_i + w_j}\right) , \qquad (1)$$

where R_{ij} represents the chromatographic resolution for components i and j, t_r is the retention time, and w represents the time-based distance intercepted along the baseline by tangents through the points of profile inflection. The basic description of resolution in physico-chemical terms [47] is written as

$$R_{ij} = \frac{\sqrt{n_j}}{2\left(1 + \frac{w_i}{w_j}\right)}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_j}{1 + k_j}\right) , \qquad (2)$$

where n_j is the number of theoretical plates corresponding to component j, α is the relative retention, and k_j is the partition ratio for the j component.

For solutes not subjected to distorting or biasing effects during migration (see Appendix B), the chromatographic efficiency can be measured from the properly recorded output signal, and thus related to the basic chromatographic variables [48] or characteristics. Specifically, chromatographic efficiency is defined in terms of height equivalent to a theoretical plate, H, and is written as

$$H \equiv \frac{d(\sigma_z)^2}{dz} = \frac{Lw_h^2}{8(\ell n 2)t_r^2} , \qquad (3)$$

where σ_z is the standard deviation of the solute zone, z is the distance along the column axis, L is the column length, and w_h is the zone width at half height.

In addition to measurements of efficiency and resolution, test procedures have been developed for evaluating the performance of glass and fused silica OTCs. These procedures are still evolving [49-53], and methods are being developed which address some of the more subtle characteristics of OTCs, e.g., catalytic activity, selective adsorptivity, etc.

Early experiments [54] tended to indicate that H, the height equivalent to a theoretical plate, was a function of column length; however, that has been found to be incorrect. Recently, experimental evidence [55-56] has shown that H can be independent of column length, and that it is relatively easy to optimize the gas flow for a chromatographic column under isothermal conditions. However, different carrier gases will exhibit a different optimum linear gas velocity, and this must be determined experimentally. Experimental data indicate no clear preference for any particular carrier gas with respect to isothermal gas chromatographic efficiency. Yet, there is an advantage in using hydrogen (and to a lesser extent helium) for high-resolution gas chromatographic work [57,58]. With these light carrier gases (hydrogen and helium) the solute zones can

be passed through the column at a higher linear velocity, thereby producing larger instantaneous concentrations at the column exit (see Appendix A). The advantages of hydrogen or helium carrier gases are especially evident in programmed temperature work with long OTCs. In addition, efficiency losses due to a programmed variation in column temperature are minimized with the use of hydrogen carrier gas. (Caution: certain protective measures should be undertaken when using hydrogen as a carrier gas in an HRGC instrument.)

There is valuable diagnostic information in the early portion of chromatograms of jet fuels, the volatile fractions of a crude oil, or shale oil. In fact, this region may presently be the most informative portion of a chromatogram in revealing unique properties or characterizations of various samples. There are three ways of improving chromatographic resolution for these early eluting volatile species. One approach is to merely cool the column oven to a temperature near ambient and maintain an extended isothermal hold period for the early emerging species. Another is to use OTCs with a relatively thick film, thereby increasing the resolving power for the more volatile components of the mixture. The third approach is cryogenic temperature-programmed gas chromatography. For this procedure, the GC instrument must be equipped for subambient operation. Eventually, the GC oven will be temperature programmed to higher temperatures to elute the higher boiling sample constituents.

In subambient programmed temperature HRGC, potential problems are associated with a change in state of the stationary phase and the associated slow mass transfer of solute molecules at lower temperatures. Consequently, care is needed in the selection of the OTC stationary phase. Recent experiments conducted in the Thermal Analysis Laboratory at the University of Dayton have shown that certain silicon gum phases (SE-30 and SE-52, have glass transition temperatures of approximately -110°C. Therefore, these stationary phases would be especially suited for subambient programmed temperature GC. Phases that readily crystallize should not be used at cryogenic temperatures. For

strict gas-liquid partitioning chromatography, a stationary phase should not be used below its glass transition temperature.

The new fused silica OTCs have polyimide outer coatings that can withstand a 350°C air environment for long periods. However, many of these coating materials exhibit glass transition temperatures of approximately -40°C. Nevertheless, these outer protected fused silica OTCs have been subjected to cryogenic trapping procedures wherein short lengths of the coiled tubing were placed in Dewar flasks containing liquid nitrogen [59] at approximately -196°C. Apparently, no difficulties (e.g., surface cracking and column breakage) were encountered in these severe low-temperature exposures. Consequently, it would seem that fused silica OTCs can be used in gas chromatographic systems designed for occasional cryogenic temperature programming use where initial temperatures may be as low as -100°C.

Undoubtedly the major attributes of HRGC are its ability to separate complex mixtures, its speed in performing separations, and its ability to obtain analytical quantitations for separated constituents. Gas chromatography can also supply qualitative data by using the Kovats retention index system [60,61] for identifying the various emerging solute zones. This system is widely used for isothermal chromatographic determinations [62]. For whatever mode of GC operation, standard tests must be conducted periodically to validate the Kovats indices information, in exactly the same manner as the routine retention data collection. For example, if the chromatographic data are obtained in a certain programmed temperature GC mode, the retention index data should be determined in that same mode of operation using internal standards.

3. ADVERSE BEHAVIOR ASSOCIATED WITH THE SEPARATION COLUMN

An important topic relative to HRGC and the generation of analytical data (quantitative and qualitative) is elution zone profile. The complete HRGC system must be capable of migrating

and eventually recording symmetrical concentration zone profiles [63]. As stated in Section IV, this performance criterion must be met before extensive sophisticated analytical work is undertaken. Causes of recorded zone profile asymmetry can originate in:

(a) the chromatographic inlet assembly,

(b) the separation column itself,

(c) the nonuniformities associated with the column and its installation, or

(d) the subsequent physical components and data-handling procedures downstream of the chromatographic column.

The reasons why asymmetric elution behavior is so detrimental to chromatographic performance, particularly with respect to HRGC, must be understood. Specifically, if elution profile distortion, e.g., peak tailing, is observed in the recorded output of a properly designed and responsive GC instrument, some entity within the system is biasing the chromatographic passage [63-66] of solute molecules. Such behavior indicates either (a) disturbances or nonuniformities in the gas flowpath which cause this bias in migration, (b) certain types of adsorptivity which can be either reversible or irreversible, or (c) chemical degradation during solute transport. In any event, this peak tailing behavior is undesirable, as it adversely affects the measured concentration of the eluting solutes. It also changes the occurrence, in time, of the concentration profile cresting of the individual solute zones.

Other types of asymmetric elution behavior are associated with admitting too much solute to the chromatographic system and thus overloading the separation column. This usually generates a profile that has its concentration centroid emerging at a time somewhat different than the elution profile crest, i.e., the zone's maximum concentration. This again would produce erroneous qualitative data.

Figure 9 shows the loss in resolution attributed directly to asymmetric elution zone profiles. The upper set of elution peaks consists of a single Gaussian profile and an exponentially modified Gaussian (EMG) profile. These two distribution profiles differ only in that the EMG response curve contains a fixed exponential tailing component which has been convoluted with the previous Gaussian profile (shown in the upper left corner). The bottom set consists of two equally spaced component elutions of Gaussian and EMG behavior, respectively. The extent of overlap for compounds i and j in the lower right-hand figure clearly shows the loss in resolution directly related to asymmetric elution behavior.

At this point in the discussion of adverse behavior associated with an OTC, it is appropriate to present a case where chromatographic peak tailing occurred as a result of physically contaminating the early regions of the chromatographic flowpath. The chromatogram of normal paraffins, shown in Figure 10, was obtained after a "dirty" and inappropriate sample had been injected into an OTC gas chromatograph. (Notice the tailing of the early solute peaks.) The previously injected sample consisted of a complex mixture of aromatic hydrocarbons, a variety of organic acids, a small quantity of low-molecular-weight polymers, some micro-size particulate, and other carbonaceous materials. In effect, this dirty sample contaminated the interior surfaces of the injector and the localized stationary phase in the inlet region of the OTC. Subsequently injected solutes (shown in Figure 10) were subjected to adsorption, biased migration, and possibly even catalysis by the contaminants residing in both the injector and the inlet region of the chromatographic column. Therefore, by merely cutting off the first ten centimeters of the column, cleaning and deactivating the injection port surfaces, and reconnecting the column, the improved chromatogram shown in Figure 11 was obtained. This particular case is one example of how the performance of high-temperature OTCs can be impaired.

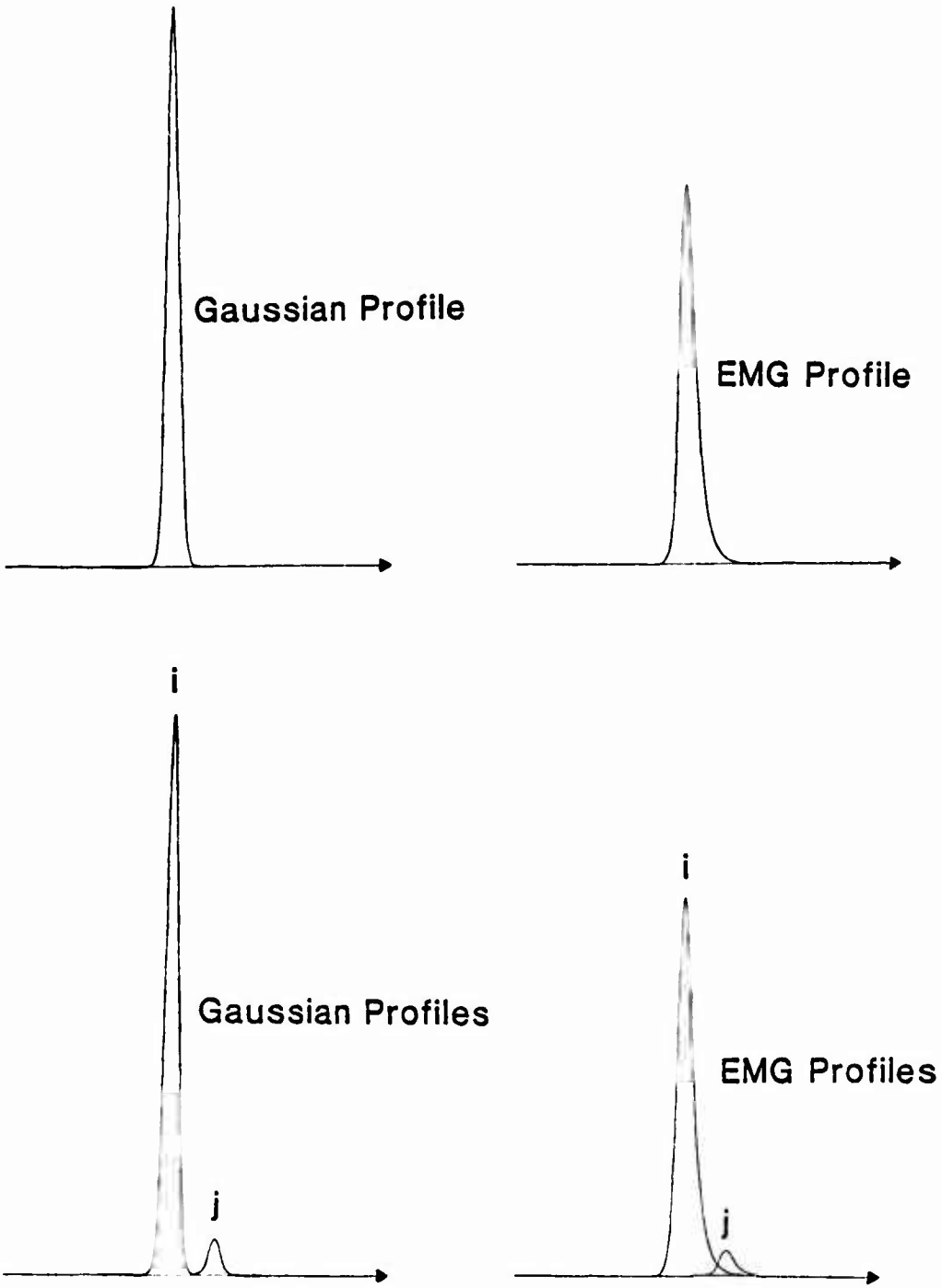


Figure 9. Gaussian and exponentially modified Gaussian elution zone profiles.

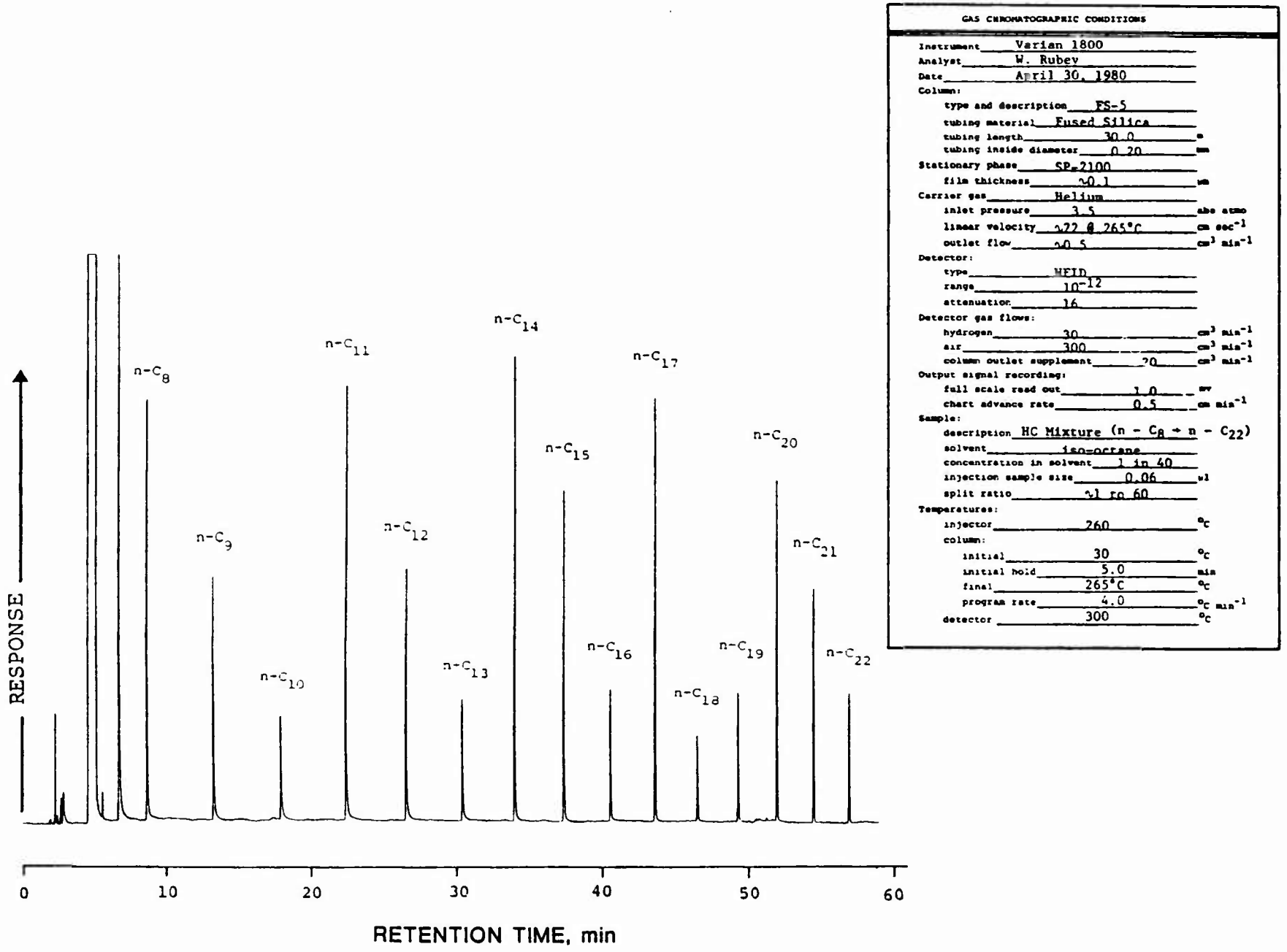


Figure 10. Series of normal paraffins eluted from a contaminated column.

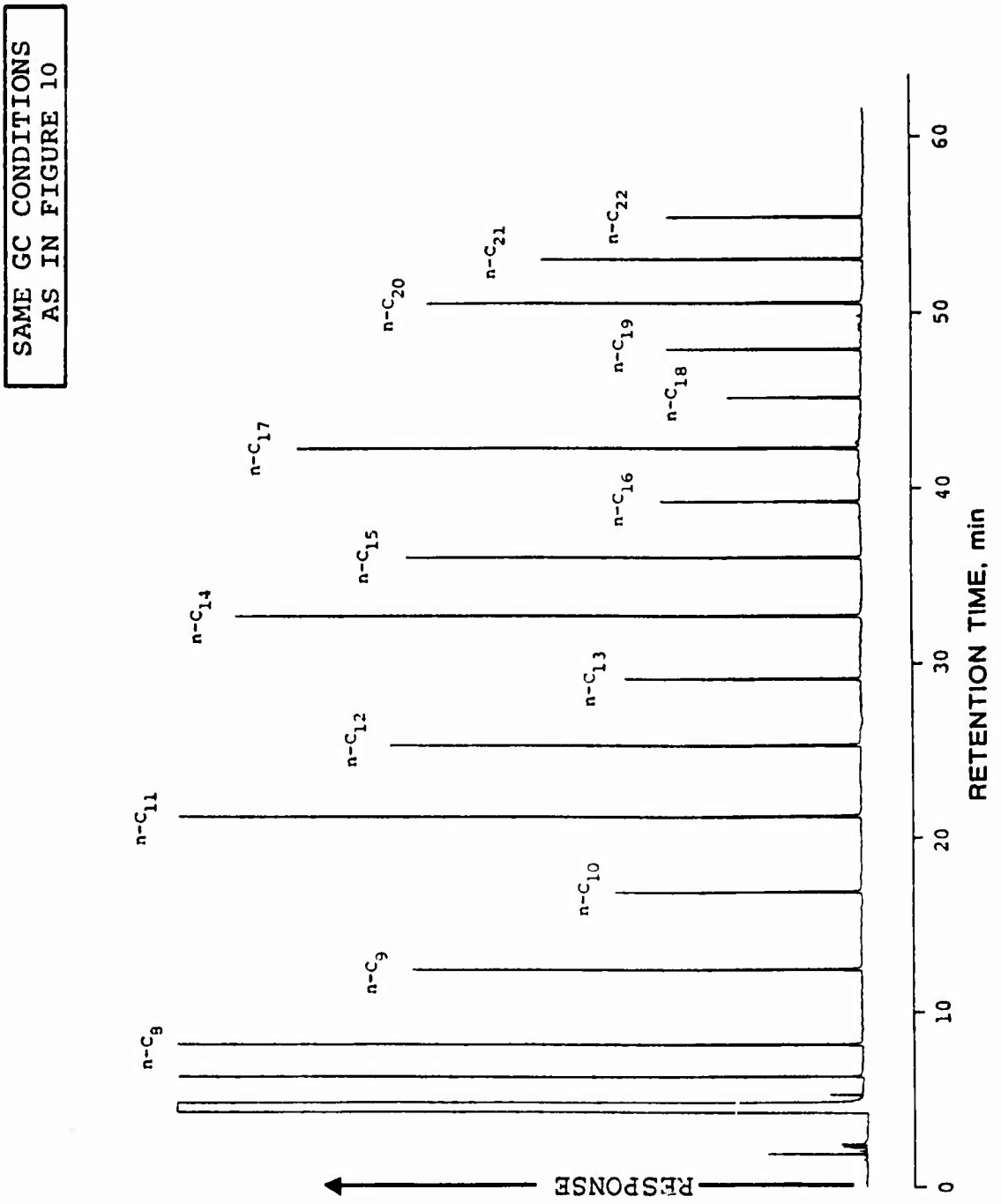


Figure 11. Elution behavior after removing contaminated section of column.

Another type of peak asymmetry has been observed recently, and the cause of this unusual form of tailing behavior is not fully understood. Figure 12 shows two partial chromatograms, one representing the elution of a chlorinated pesticide, the other showing the elution profile of a nitrophenol. In some chromatographic systems, similar types of tailing behavior have been observed even for hydrocarbons. Basically, this asymmetric behavior is characterized by a prolonged baseline elevation after the elution of a certain solute. This distinct elevation of the baseline is not related to electronic offset or recorder deadband. In the past, comparable results were observed when water was eluted through a chromatographic column. Similar behavior [67] has been observed with a dirty detector or foreign deposits in the detector region (deposits that introduce selective solubilities or adsorptivities).

Although there are several theories concerning this phenomenon, none of the explanations is totally satisfactory. This type of asymmetric elution behavior can have serious consequences. For example, there is the question of whether the adsorptivity is reversible or irreversible, and if it is reversible, whether the solute molecules will elute in time to be included as part of the detected solute zone. There is also the question of whether the adsorptivity is concentration dependent, such as the undesirable GC quantitative behavior as characterized by Figure 13.

In some instances, nonquantitative transport (that is, irreversible adsorptivity) can occur even if the emerging solute zone profile is symmetrical. On the trace concentration level, there are retardation mechanisms that would not necessarily produce the telltale asymmetric elution profiles.

4. OVERLOADING OF AN OPEN TUBULAR COLUMN

With a HRGC system, it is possible to trade-off and compromise on resolution, analysis time, and sample capacity. Basically, this three-component compromise is available in most

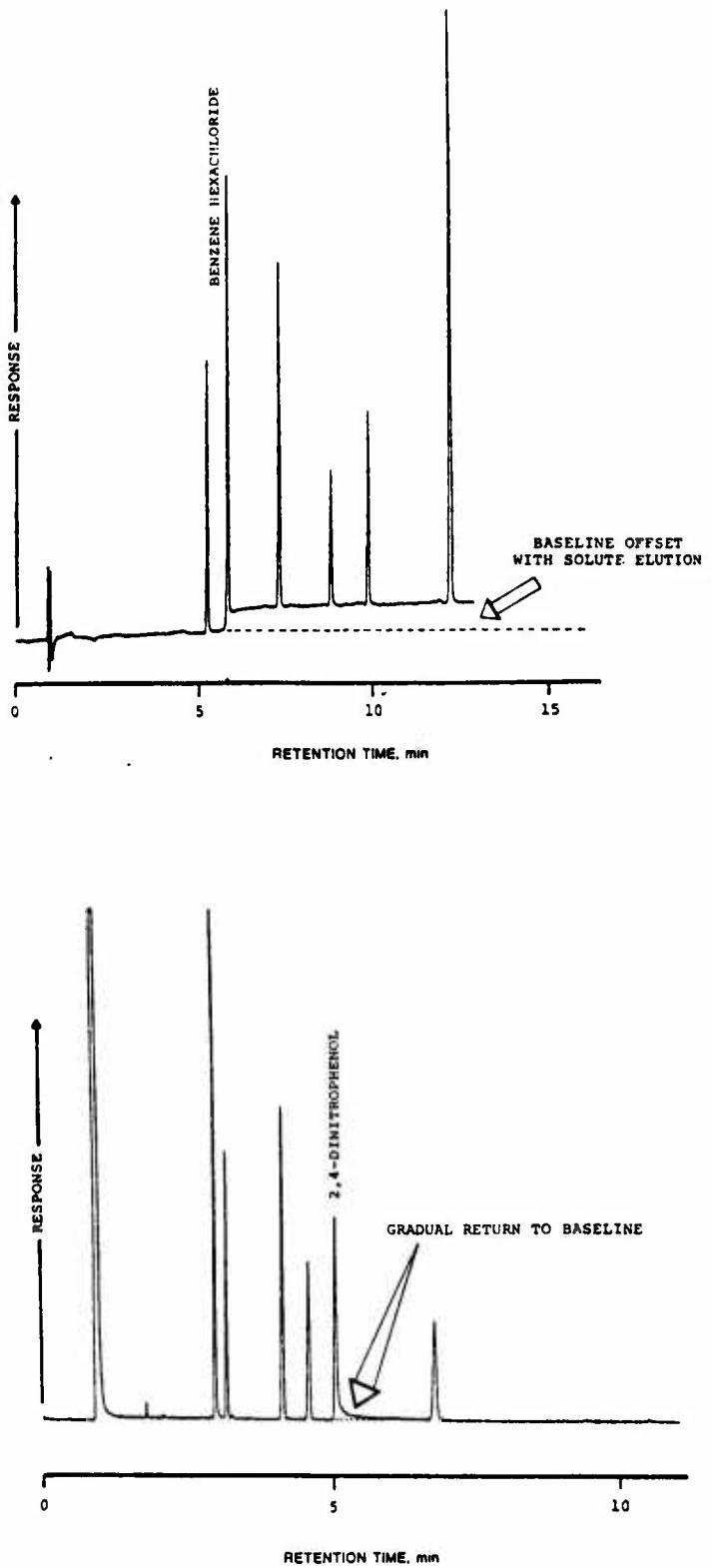


Figure 12. Open tubular column gas chromatograms that exhibit unusual baseline behavior.

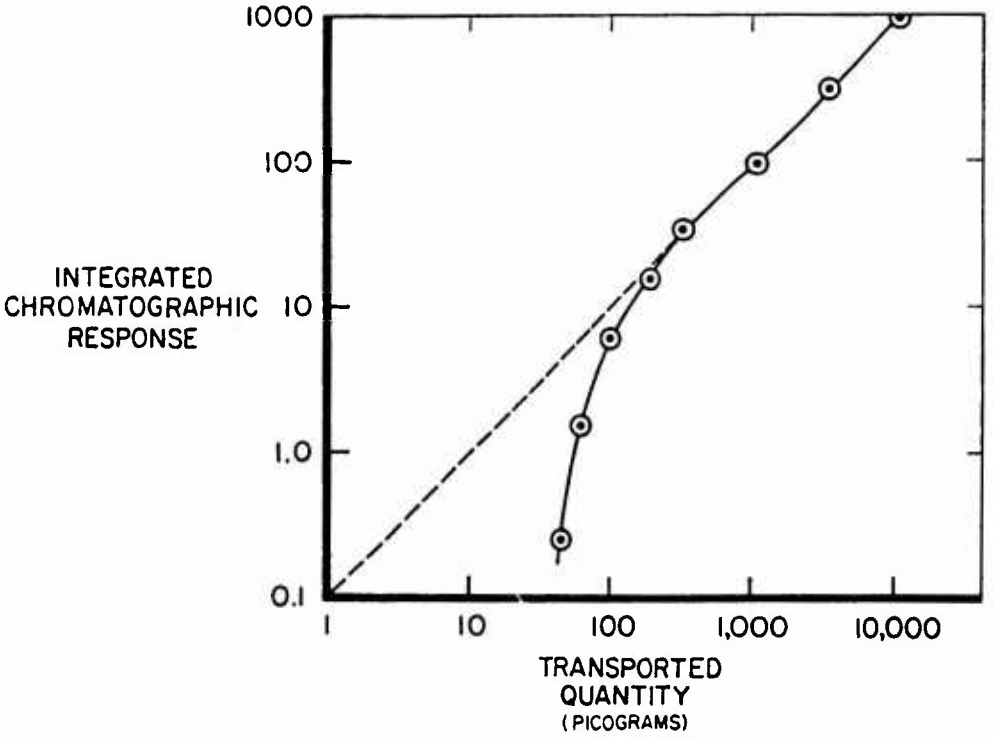


Figure 13. Undesirable quantitative behavior.

of the chromatographic techniques. Figure 14 shows a triangular relationship relating resolution, analysis time, and sample capacity. Quite simply, the analyst can enhance any of these operational attributes, but at the expense of one or both of the other attributes. For example, if the maximum possible resolution is sought, it will require a long analysis time, and it will have to be accomplished with a small quantity of admitted sample.

It is increasingly clear that sample capacity is important in HRGC, for if too small a sample is admitted to the instrument, there is a problem in detecting the low level components. And if too large a sample is admitted to the chromatographic column, overloading will occur.

Gas-liquid chromatographic column overloading has been well known [68] for almost two decades. Although overloading phenomenon has been recognized and studied, it does not lend itself to precise characterization for a given chromatographic system and a given sample. Recent authors have addressed this topic [69,70] and some researchers consider column overloading in chromatographic dynamic terms, e.g., localized velocity concepts.

The relationship between the zone variance of an emerging solute profile and the quantity of solute admitted to a given chromatographic column can be expressed in an approximate generalization as shown in Figure 15. This is a hypothetical curve, and certainly this relationship would vary with the dimensions and characteristics of the separation column and the admitted solute. Even so, if too much solute is injected into the chromatographic column, an overloaded condition will exist and the emerging solute zone will be broader than if the chromatography were performed in a nonoverloaded manner.

In the overloaded condition, the emerging solute zone is not only broader but is also skewed. In practically all cases, the crest value of the emerging solute zone will emerge later in the overloaded condition than in nonoverloaded chromatographic zone migration. This can present serious problems in generating

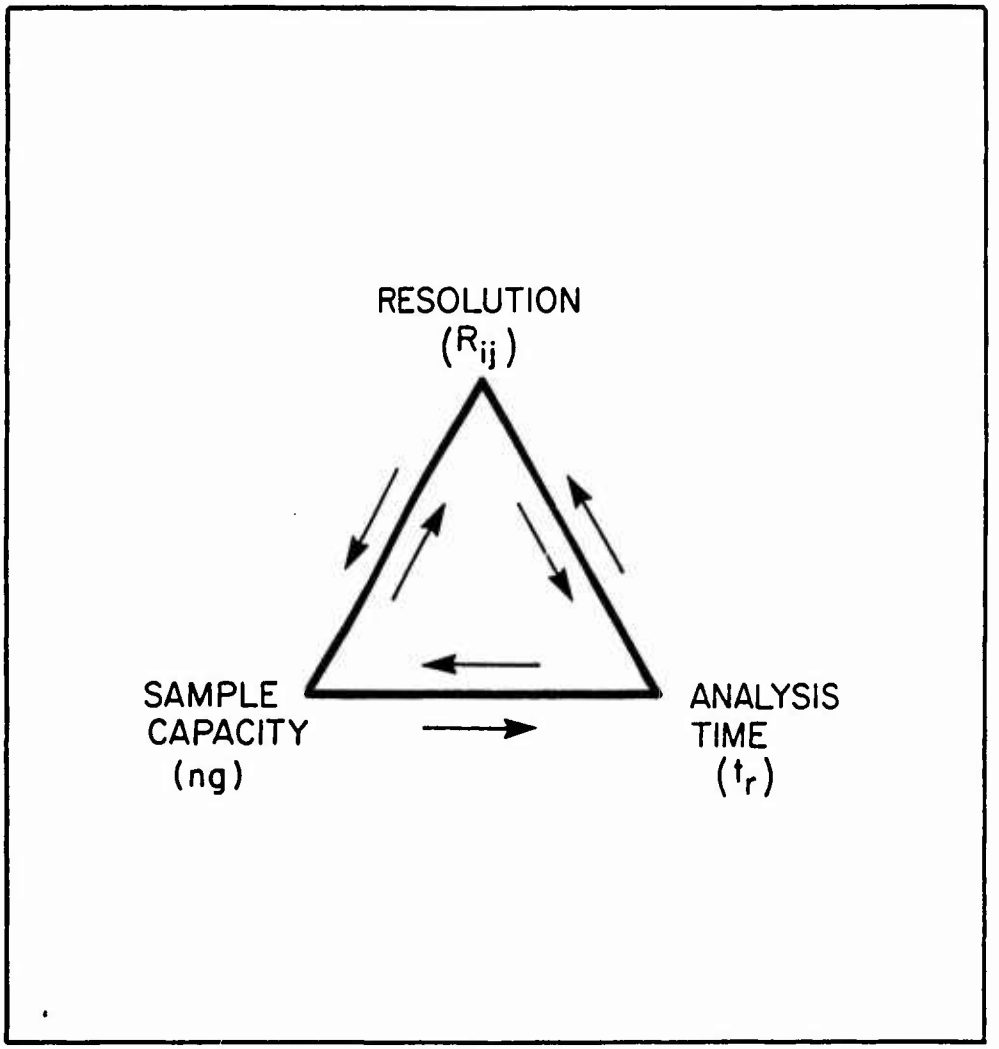


Figure 14. Relationship of three-component gas chromatographic compromises.

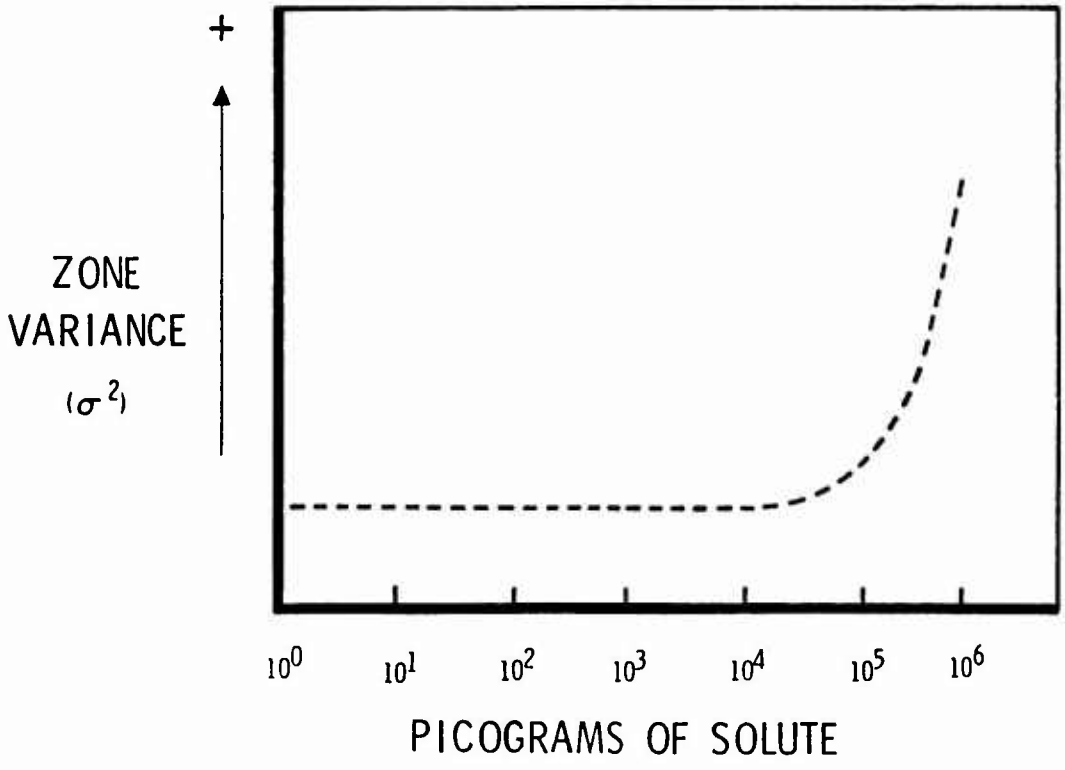


Figure 15. Relationship of admitted solute versus solute zone variance.

qualitative data, specifically when characterizing the eluting solutes using the Kovats retention index procedure. Accordingly, when the objective is to generate precise qualitative information, it is imperative that the emerging solute zones not be overloaded. (Appendix B shows that the peak apex can be used as an indicator of the emergence of the solute zone centroid, provided the solute zone is symmetrical.)

There are many procedures for measuring elution zone profile asymmetry and Figure 16 illustrates six graphic procedures for obtaining zone asymmetry measurements (see reference [63] for a detailed description of some of these profile characterization procedures). The measurement procedure as introduced by Haarhoff, et al. [71] was selected for measuring the zone asymmetry of a series of hydrocarbons that eluted from a particular HRGC column.

A hydrocarbon mixture which was prepared contained equal weights of normal undecane, normal dodecane, and 2,6-dimethyl undecane. Different weights of the mixture were placed in an iso-octane solvent and a small amount of naphthalene was added to each of the prepared samples. These samples were injected into a high-resolution gas chromatograph containing a 60-meter-long fused silica OTC. This particular column had a dimethyl silicone film thickness of approximately 0.25 microns. The chromatographic conditions for this overloading experiment are presented in Figure 17. The weights of the hydrocarbons admitted to the OTC ranged from 2 ng to 256 ng each. The quantity of naphthalene admitted during this series of tests never exceeded 4 ng.

One objective of this experiment was to determine what effect the normal paraffin overloading would have on the Kovats retention index of the nonoverloaded naphthalene. These tests were run under isothermal conditions of 140°C, and examples of partial GC tracings are shown in Figure 18. It can be seen that the upper tracing corresponds to an overloaded condition (skewed profiles) for the three components injected in large concentration; however, the small quantity of naphthalene is not overloaded. During the

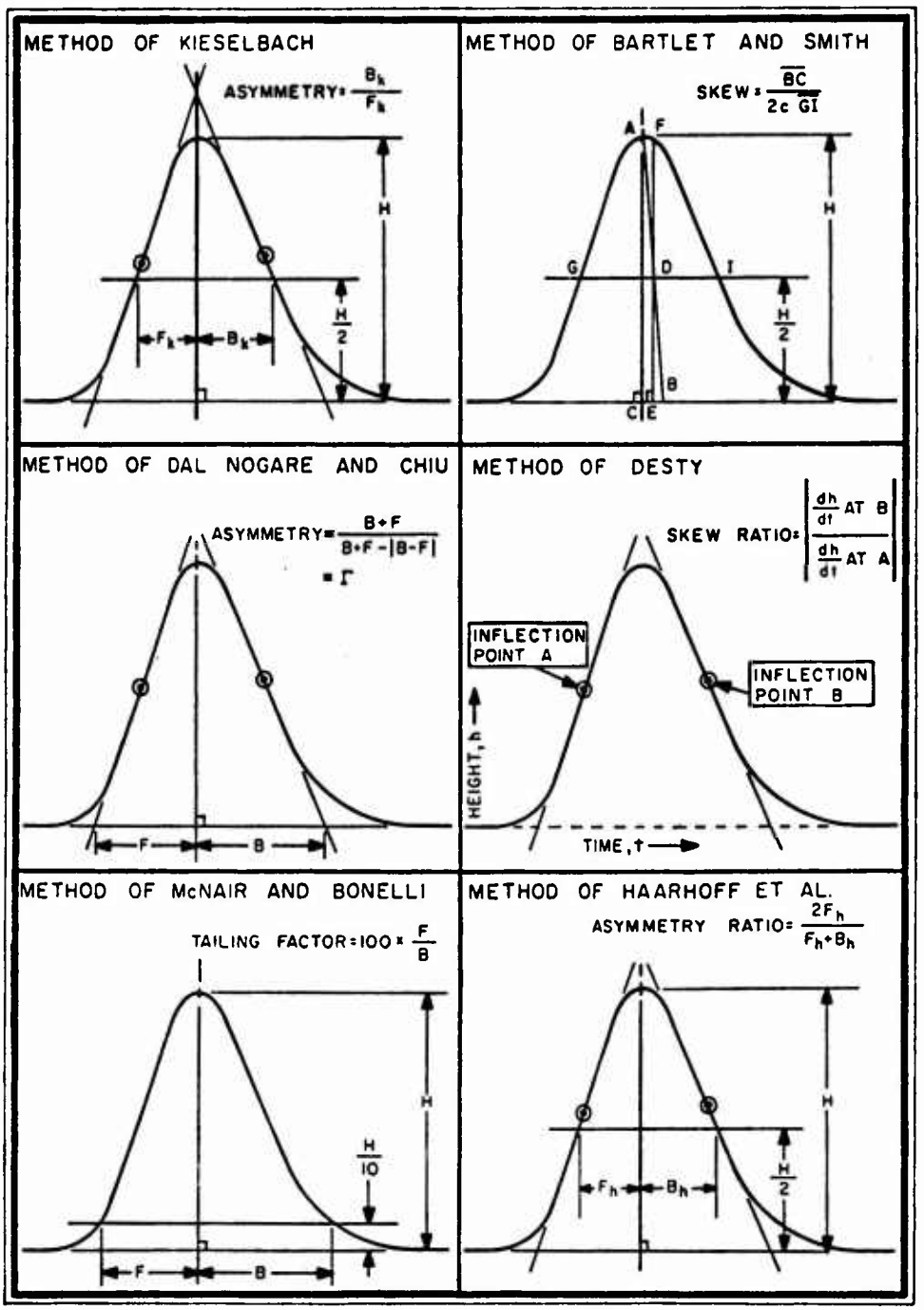


Figure 16. Graphic procedures for measuring solute zone asymmetry.

GAS CHROMATOGRAPHIC CONDITIONS

Instrument: Varian 1800
Analyst: W. Rubey
Date: 7-23-80
Column:
type and description: WCOT
tubing material: Fused silica
tubing length: 60 m
tubing inside diameter: 0.25 mm
Stationary phase: SE-30
film thickness: 0.25 μm
Carrier gas: Helium
inlet pressure: 3.7 abs atmo
linear velocity: ~28 cm sec^{-1}
outlet flow: ~1.7 cm^3 min^{-1}
Detector:
type: HFID
range: Noted
attenuation: Noted
Detector gas flows:
hydrogen: 30 cm^3 min^{-1}
air: 300 cm^3 min^{-1}
column outlet supplement: 20 cm^3 min^{-1}
Output signal recording:
full scale read out: 1.0 mv
chart advance rate: 10.0 cm min^{-1}
Sample:
description: $n\text{-}C_{11}$, $n\text{-}C_{12}$, 2,6 DMUD & NAPH.
solvent: $i\text{-}C_8$
concentration in solvent: Noted
injection sample size: 1.0 μl
split ratio: ~1 to 33
Temperatures:
injector: 240 °C
column:
initial: 140 ITGC °C
initial hold: --- min
final: --- °C
program rate: --- °C min^{-1}
detector: 300 °C

Figure 17. Chromatographic conditions for solute overloading experiment.

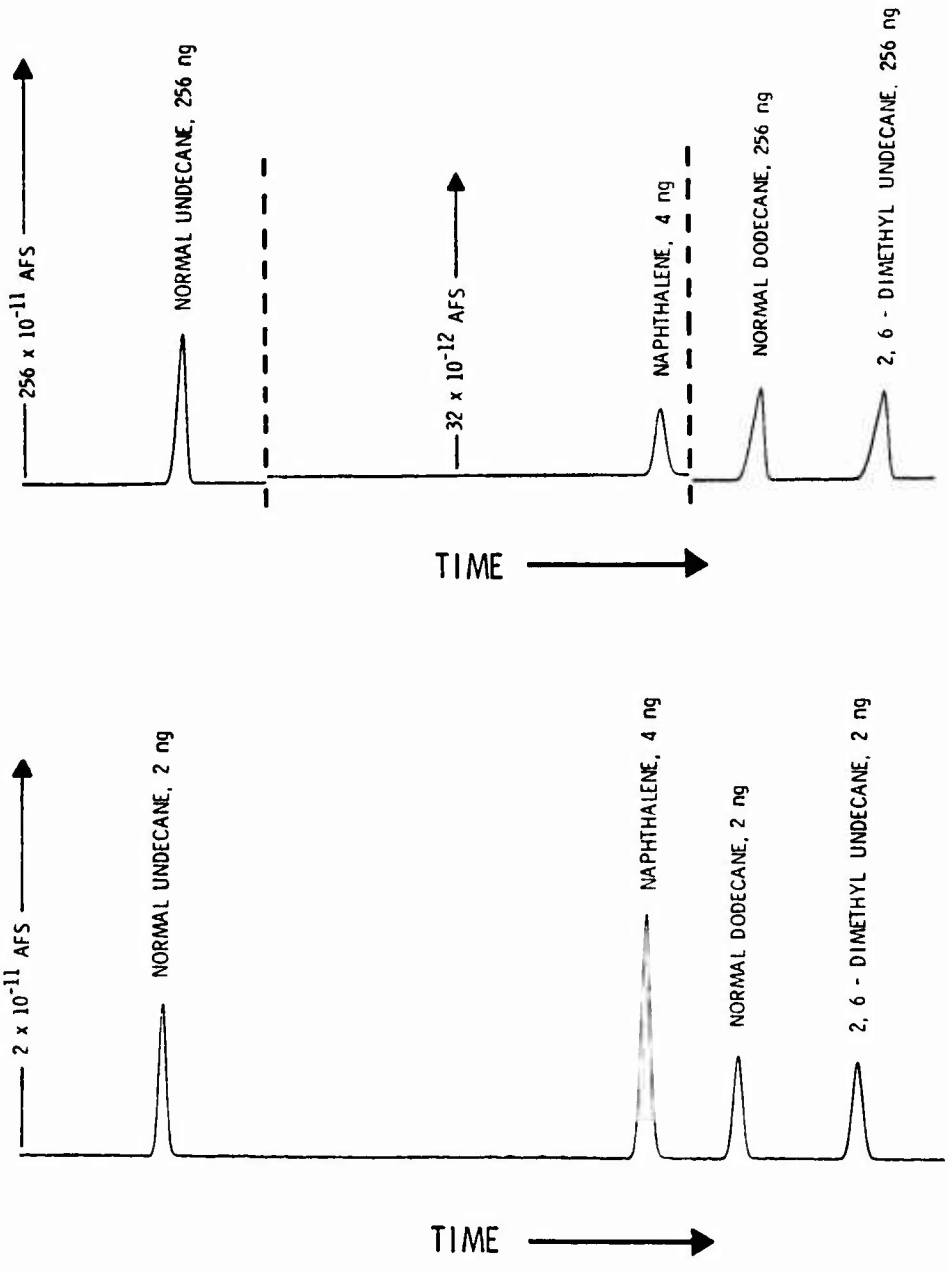


Figure 18. Examples of partial chromatograms from overloading experiment.

elution of these four components, the chart advance rate on the chromatographic recorder was increased so that symmetry measurements could be made using the graphic measurement technique of Haarhoff, et al.

The data resulting from this series of tests are presented in Table 3 and this information is also presented graphically in Figure 19. It is apparent from Figure 19 that asymmetric behavior is pronounced, once the sample size exceeds approximately 50 ng. Here again, this overloading information applies only to a particular series of solutes and a given HRGC column. However, this information corresponds to recommendations [72] that the maximum acceptable solute quantity that should be admitted to a thin film OTC (if GC qualitative data are to be obtained) is approximately 100 ng. Table 3 shows that larger quantities of solute would dramatically affect the Kovats index value, I_D^a. In this experiment, the standards for the Kovats index, specifically the normal undecane and the normal dodecane, were overloaded, but the naphthalene at no time experienced overloaded elution behavior.

Another factor relative to column overloading is that the temperature of the column has a pronounced effect upon overloading, and thus, on acceptable sample capacity. For practically every class of organic compound, the lower the gas-liquid chromatographic column temperature, the greater the sample capacity.

TABLE 3

EXPERIMENTAL DATA PERTAINING TO SOLUTE OVERLOADING

On Column Solute Weight (ng)	Asymmetry, A_s (n-C_{11})	(n-C_{12})	(2,6 DMUD)
256	1.29	1.53	1.56
128	1.13	1.40	1.43
64	1.07	1.21	1.25
32	1.04	1.13	1.16
16	0.99	1.05	1.09
8	0.98	1.03	1.05
4	0.98	0.98	1.03
2	0.99	1.00	1.01

On Column Solute Weight (ng)	SE-30 $I_{140°C}$ naphthalene		$\lvert\Delta I\rvert$
256	1183.84		1.60
128	1184.38		1.06
64	1185.06		0.38
32	1185.42		0.02
16	1185.49		--
8	1185.40	$\bar{I}$=1185.44	--
4	1185.51	σ=0.075	--
2	1185.35		--

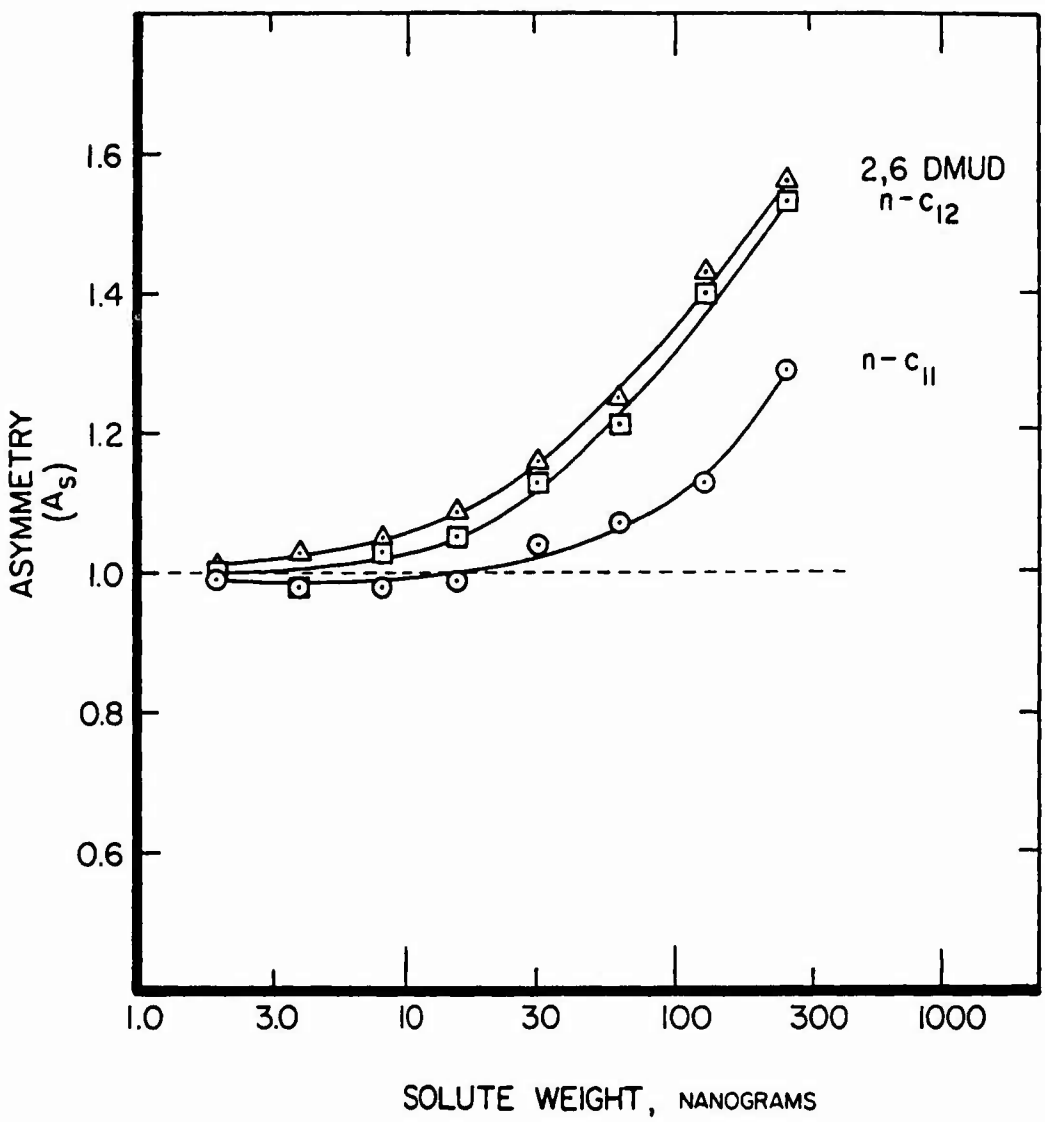


Figure 19. Measured zone asymmetry versus quantity of solute.

SECTION VII

UNIFORM TRANSPORT AND EFFLUENT DETECTION

Once a sample has been admitted to a high-resolution gas chromatographic system, it must be quantitatively transported through the flowpath and eventually each of the various constituents of the sample must be detected and properly recorded. The previous section discussed in some detail the requirements of a HRGC column. This section addresses the transport criteria that apply to both the column and the detection region of a HRGC system.

1. UNIFORM TRANSPORT CRITERIA

There are basically three criteria for the quantitative transport of stable gas-phase substances in HRGC. First, it is necessary to have material uniformity throughout the gas flowpath. For example, the tubing material and the wall structure must be homogeneous and smooth, and they must exhibit the same thermal conductivity throughout. This material should be hardy with respect to physical handling and it must be capable of withstanding high temperatures. It is essential that the entire flowpath contain no adsorptive or catalytic surfaces.

Second, the localized gas phase should be homogeneous with respect to internal pressure and internal temperature. A gas chromatographic flowpath can tolerate a miniscule negative temperature gradient along its axis, and in some cases this is even preferable [73]. However, in no situation should there be cyclic thermal oscillations along the length of the column. Of course, in HRGC there will always be a slight negative pressure gradient due to the compressibility of the mobile phase.

Third, there must always be a constant velocity of sweeping gas throughout the HRGC flowpath. That is, there should not be any tubing diameter transitions, recesses where stagnant

mobile phase can reside, or cavities where unswept solute molecules can lodge. If the HRGC system conforms to these three transport criteria and if the separation column has been properly prepared, it is possible to conduct high-performance GC analyses.

The effect of column temperature variations upon solute zone migration and retention has been studied by several workers [74,75]. For the special technique of high-precision gas chromatography to be used for studying the physio-chemical behavior of different compounds, fastidious control is needed with respect to column oven temperature. Spatial temperature variations within a column oven have also been examined from a theoretical standpoint [66,76].

Early open tubular columns were prepared using highly conductive wall materials and relatively large wall thicknesses. With these OTCs, subtle variations in localized temperature did not appear to be a significant problem as any small spatial or temporal variation in temperature was apparently averaged out due to the mass and heat capacity of the column wall. Also in previous times, stainless steel OTCs were mounted on mandrels that tended to smooth out any existing unevenness in the oven temperature distribution. With the advent of very thin-wall fused silica OTCs where the wall material is only approximately 30 microns thick, increased concern has been registered with respect to both the spatial and temporal thermal nonuniformities in the vicinity of the HRGC column.

When a fused silica OTC is coiled in a cylindrical manner on a column cage (diameter approximately 140 mm) and then located within a chamber which can unfortunately generate thermal gradients, then temperature variations can be produced along the axial length of the OTC.* If temperature nonuniformities exist within a particular column oven, these variations would have the

*Several researchers [77-79] have observed such temperature variations and some have suggested procedures for dealing with them [78].

greatest effect upon relatively short OTCs that were used in the programmed-temperature GC mode. The longer OTCs would tend to dampen the effects of the thermal nonuniformities as the solute zones would be more dispersed.

Three different procedures have been used in our laboratory to eliminate the possible adverse effects of thermal nonuniformities. Figure 20 shows a 50-meter-long fused silica OTC that has been wrapped with woven glass tape (Wale Apparatus, part no. 1706). This particular column is not wound on a mandrel, and the entire coiled tubing is contained in a rather compact oval that measures approximately 140 mm in diameter. The ends of this OTC are covered with a special ceramic fiber sleeve (Omega Engineering, part no. XC-116) which terminates at the injector and the detector of the HRGC system. Figure 21 shows a similar arrangement, but in this case a 60-meter-long fused silica OTC is wound on a metal cage and then enclosed in woven glass cloth. Here again, the ends of the column are contained within lengths of ceramic fiber sleeving. The third method (see Figure 22) that has been used in our laboratory employs a separate chamber which houses an OTC wound on its column cage. This chamber, a cylindrical aluminum dish with perforated cover, is placed within the column oven thereby obtaining a high uniformity of temperature within the inner chamber. The column ends that emerge from this chamber are encompassed with the special ceramic fiber sleeving. And as with the two previous OTC installation procedures, the sleeving butts against the injector and detector connections.

These three column installation procedures have only been used with relatively long OTCs, and were intended for programmed temperature GC operation. Nevertheless, we have thus far not observed any departures from symmetrical elution profiles when examining pure normal paraffins with these column installations.

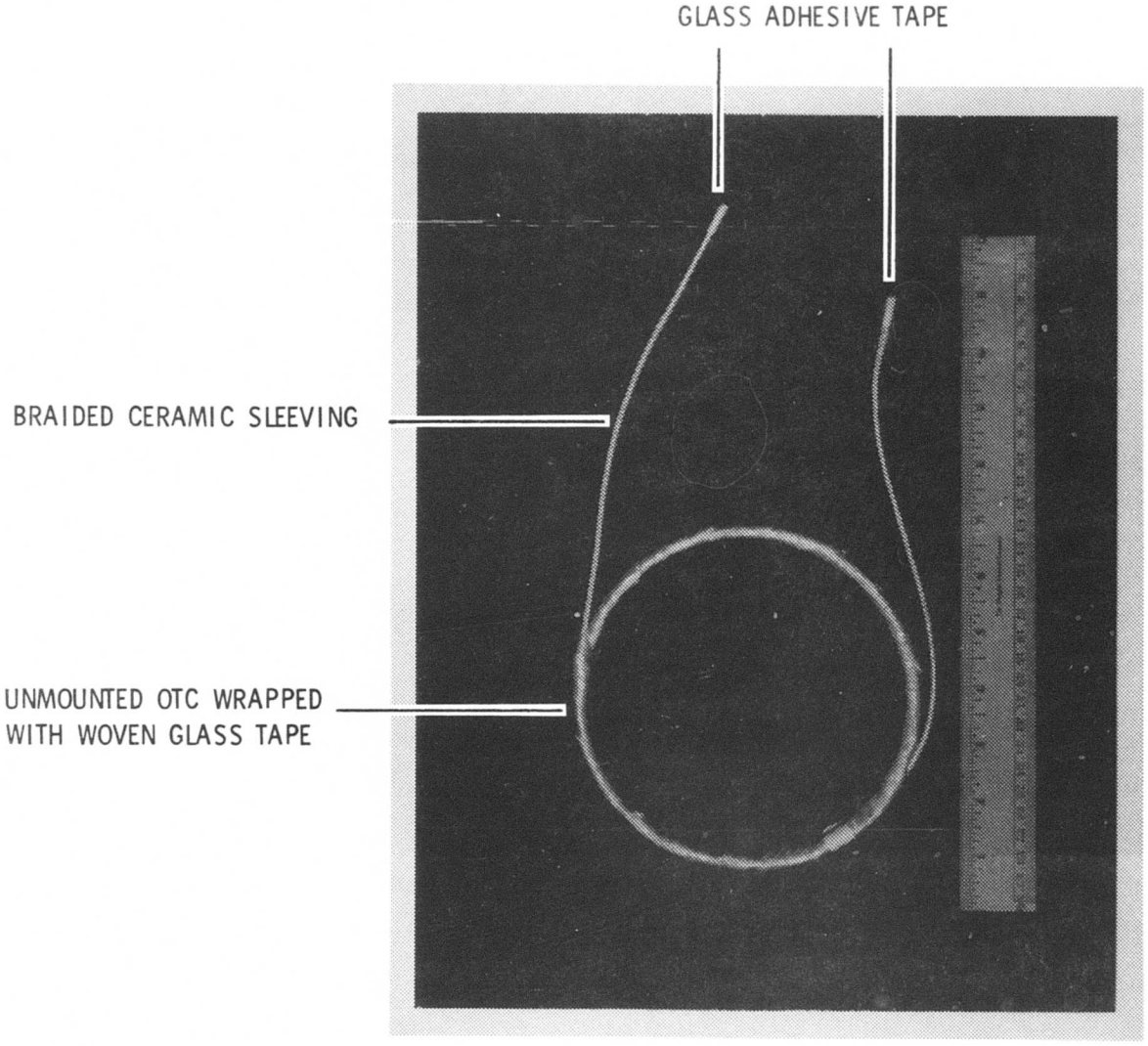


Figure 20. Fused silica open tubular column wrapped with woven glass tape (not mounted on a column cage).

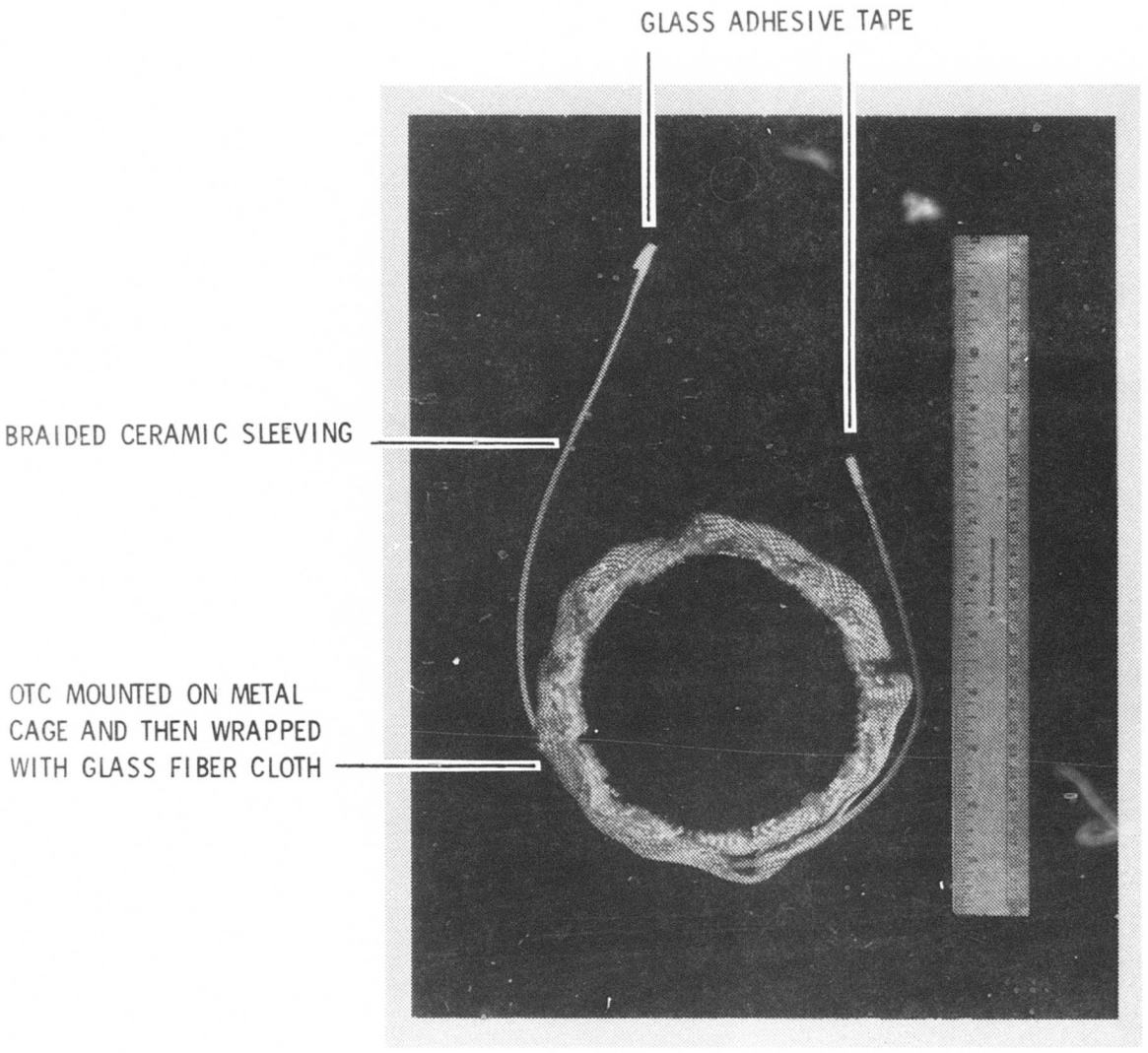


Figure 21. Fused silica open tubular column covered with woven glass cloth (column is mounted on a metal cage).

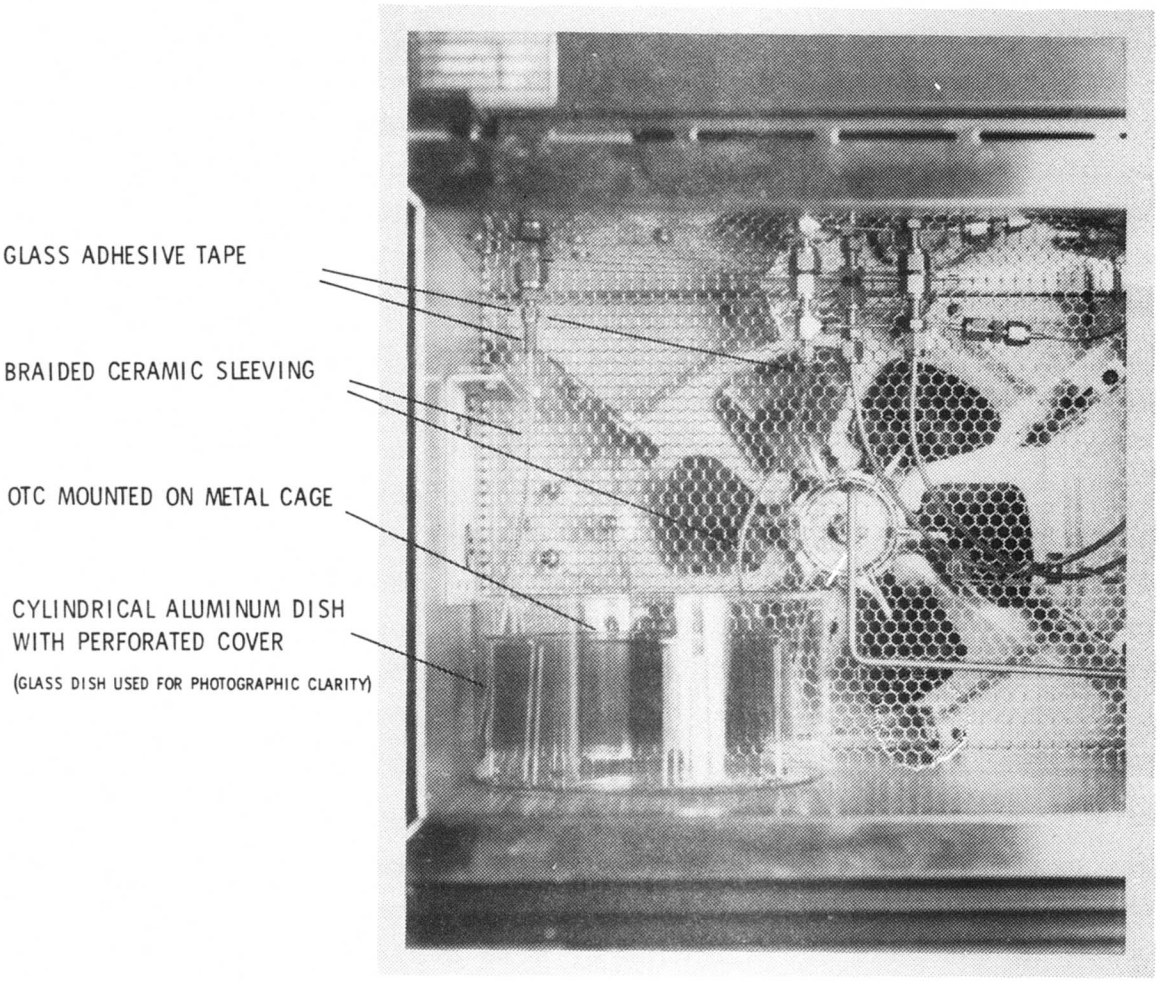


Figure 22. Fused silica open tubular column contained within a separate chamber.

2. EFFLUENT DETECTOR INSTALLATIONS

Several high-sensitivity detectors are routinely used for sensing the effluent from gas chromatographic OTCs. The hydrogen flame ionization detector (HFID) is currently the most widely used detector for conducting GC analyses with OTCs, although an increasing amount of HRGC work uses selective detectors [80-89] such as the electron capture detector (ECD), the thermionic specific detector (TSD), the Hall electrolytic conductivity detector (HECD), the flame photometric detector (FPD), the photoionization detector (PID), the ultraviolet photometric detector (UVD), various types of mass spectrometric (MS) detection devices, and Fourier transform infrared (FTIR) detection instrumentation.

Effluent detectors arranged in series connections are becoming popular. For example, an ECD has been connected upstream of an in-line HFID for obtaining selective and universal detection [90] of emerging solutes. An effluent detection arrangement recently described [91] uses a two-segment effluent splitter that sends part of the effluent to a HFID and passes the other part through a series-connected ECD and FPD. These multiple detector arrangements [92,93] provide simultaneous information on the chemical nature of emerging solutes.

It is important that the gas flow from the end of the chromatographic column to the "active" region of a detector be well defined and free from sources of zone broadening or distortion. This is a very crucial gas transport region, one overlooked in the past and slighted by some designers of currently manufactured OTC gas chromatographs.

The chromatogram shown in Figure 23 represents the problem area, by presenting a series of high-purity normal paraffins contained in an iso-octane solvent. Upon first inspection of this chromatogram, it seems that the GC instrument that generated this particular chromatographic tracing had good gas transport

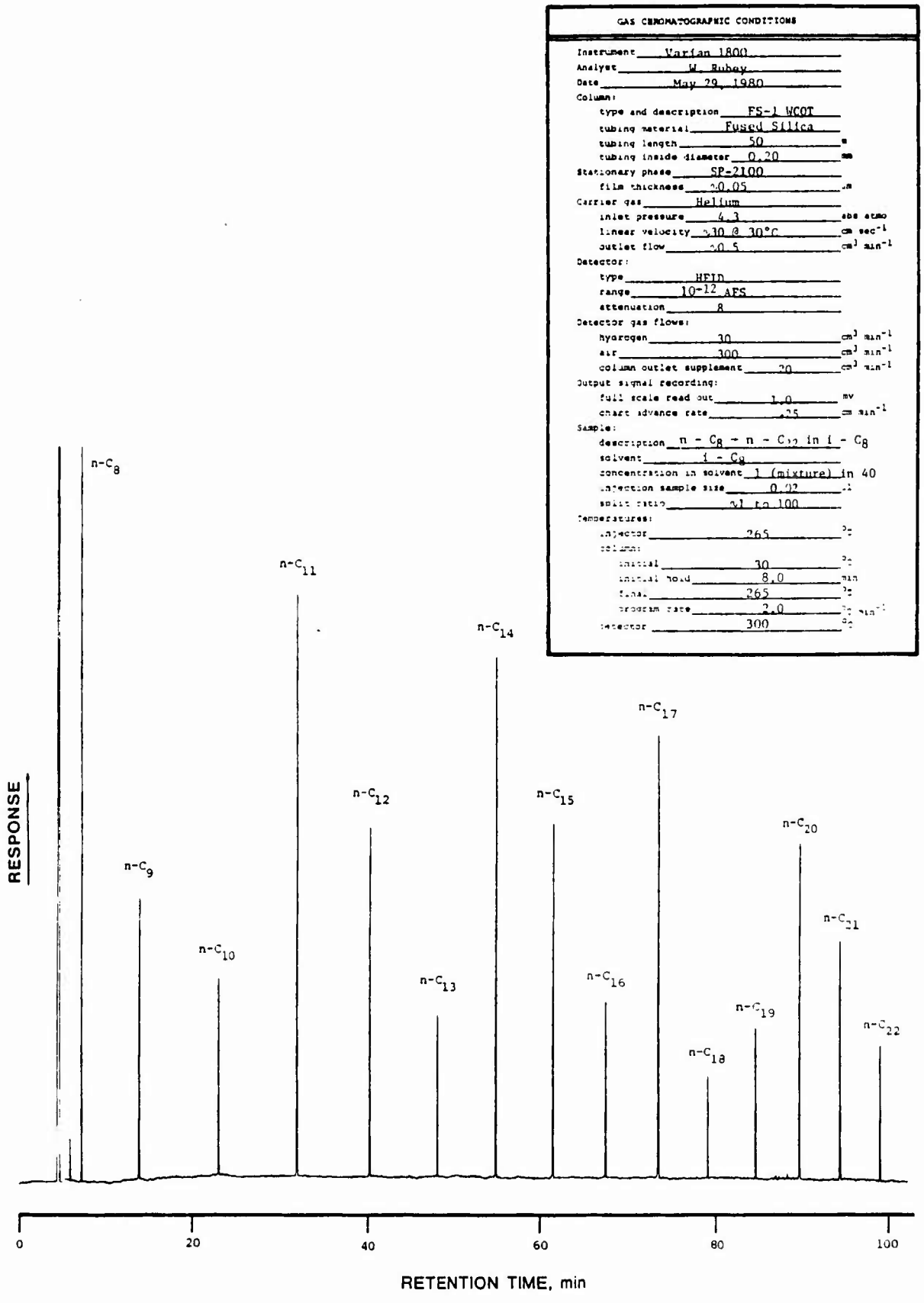


Figure 23. Open tubular column gas chromatogram of a series of high-purity normal paraffins.

properties as the emerging solute peaks appear to be almost line-functions. However, by selectively expanding the time axis of the chromatogram recording by 100X, as shown in Figure 24, it is observed that some elution zone profiles show serious departures from the smooth and symmetric Gaussian contour. Evidently, some entity or property in the chromatographic system distorted these pure solute zones. This same type of profile distortion has been observed when using both a conventional Pyrex glass wall coated OTC and a tightly wrapped fused silica OTC. In this case, the profile distortions were caused by a combination of factors originating in a transfer tube, a right-angle bend in the entry to the detector, and several simultaneous flowpath diameter transitions between the end of the OTC and the sensing region of the HFID. It is worth noting that in this case the observed subtle distortions were due largely to unpredictable mixing phenomena during transport and not to condensation or adsorption.

In elution chromatography, the shape of the emerging solute zone is important [63]. If the zone contour is distorted (e.g., gradual shoulders, multiple crestings, inflections, steps, etc.) by some form of mixing chamber, diffusion chamber, channeling device, unswept recess, or other undesirable flowpath anomaly, the analyst may conclude erroneously that there is more than one chemical species represented by the distorted solute zone. Such would have been the case for the two examples of distorted zones shown in Figure 24.

Another reason for mandating that a HRGC instrument elute pure solutes as undistorted and symmetrical profiles is that one can then use the peak height rather than peak area for certain quantitations [94,95]. The distorted profiles shown in Figure 24 would introduce error in a quantitation established by peak height. Here again, the actual time of cresting of distorted solute zones (skewed profiles) would not correspond to the same time as the emergence of the centroid of the solute zones. This source of error would affect the qualitative analysis.

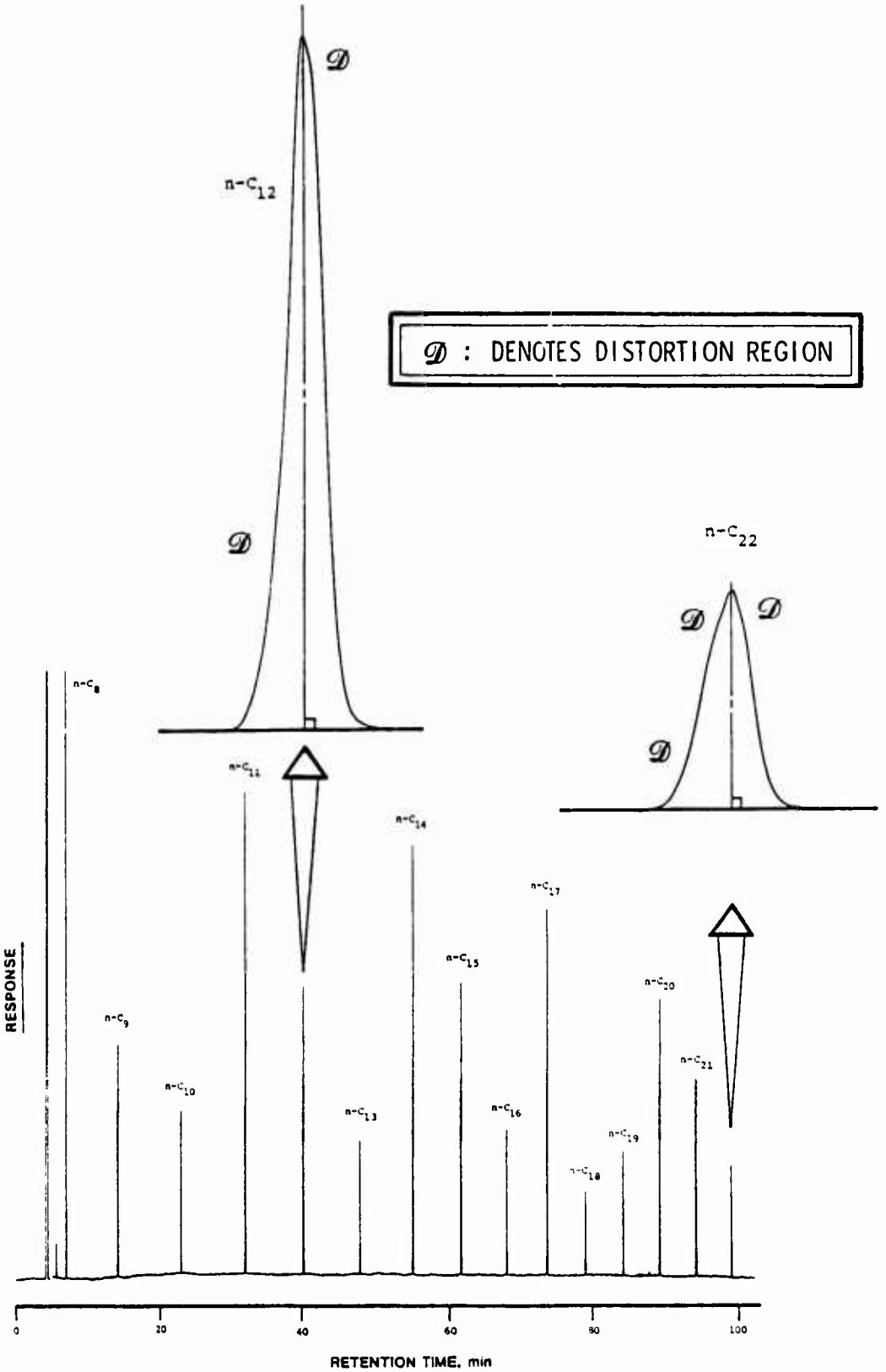


Figure 24. Distortion of pure solute zones by flowpath disturbances at column exit.

Not many years ago, it was common to use special unions for joining OTCs in series arrangements and for attaching OTCs to inlet and exit tubing connections. However, practically any type of junction, coupling (including couplings made with heat-shrink Teflon tubing), union, or butt end connector can introduce asymmetric elution profiles, exponential peak tailing, and selective adsorption, particularly if migrating solutes encounter polymeric tubing ferrule materials at these junctions (see Figure 25). The reason for this peak tailing behavior is that solute molecules are readily forced into these narrow unswept recesses by the migrating solute concentration gradient, but the only way these "captured" molecules can reenter the main flowstream is through diffusion. Darcy's Law is very clear on this point; specifically, a finite pressure drop is necessary to have fluid flow [96]. And the pressure drop across these narrow radial channels is negligible.

As a further complication, the gradual deposition of stationary phase bleed condensate into these narrow unswept recesses hinders the quantitative transport of highly retained solutes present in low concentration. Increased data scatter and behavior such as seen in Figure 13 can result from practically any junction contaminated with stationary phase.

A uniform gas chromatographic flowpath that encounters no junctions, diameter transitions, or thermal gradients from its inlet region to the point of emergence in the gas chromatographic detector is an ideal column installation. Such a model for an OTC installation has negligible extra-column zone spreading contributors. This model can be realized by straightening the inlet and exit ends of conventional thick-wall glass tubing before the tubing is fabricated into a separation column. With the advent of flexible fused silica tubing [30], such a model installation requires only the fabrication of precise adapters for making proper connections at the column entrance and at the OTC exit. Figure 26 depicts a HFID and adapter assembly designed specifically for placing the chromatographic column exit in a

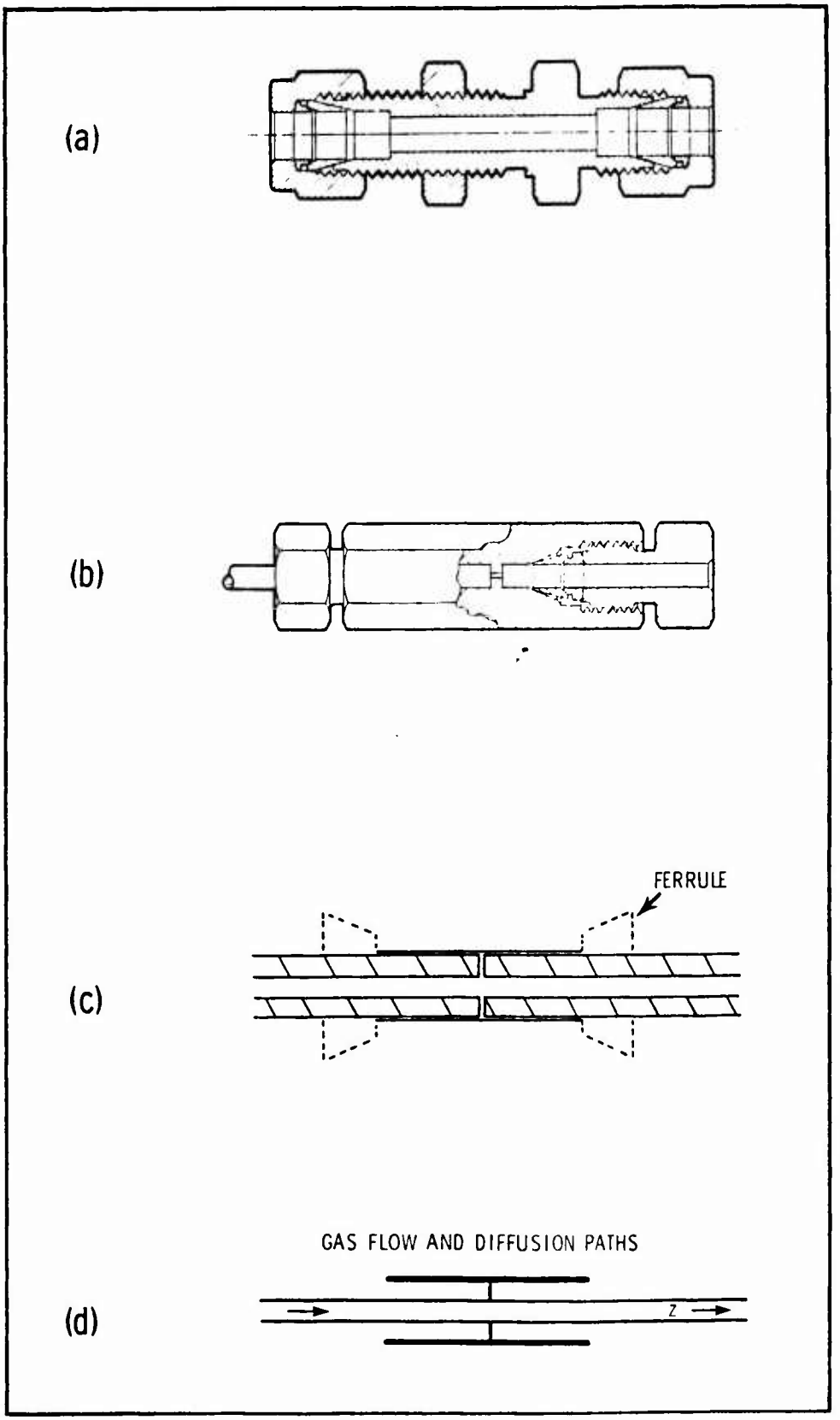


Figure 25. Tubing couplings and unions and sources of poor quantitative transport.

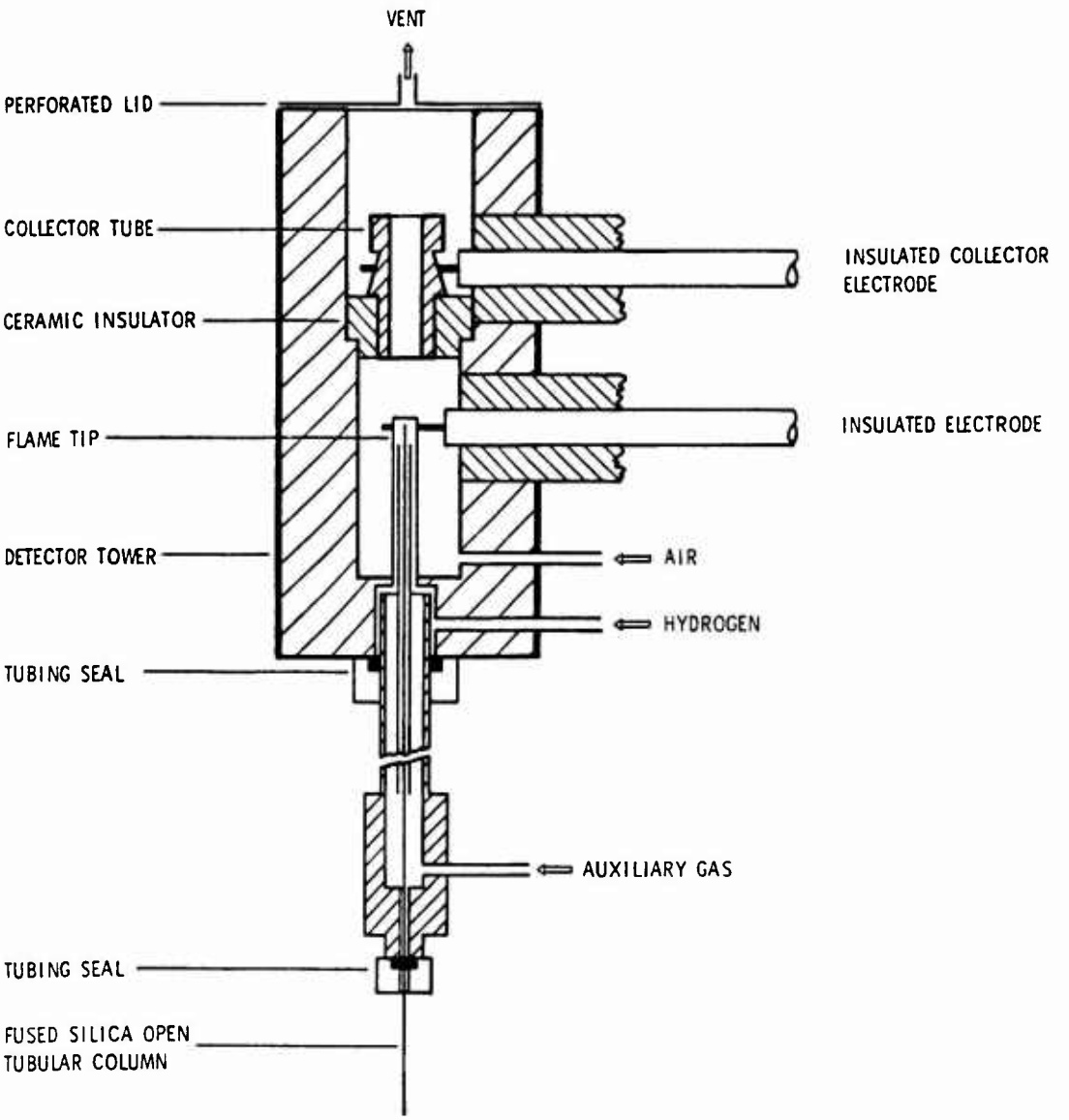


Figure 26. Schematic of a hydrogen flame ionization detector and adapter for high performance with open tubular columns.

location very close to the active sensing region of the HFID. This particular design closely follows an earlier design introduced by Gaspar, et al. [97] who were able to generate extremely precise Gaussian elution profiles using this type of detector and capillary column exit connection.

As previously stated, the HFID is now the most commonly used detection device for sensing organic solutes emerging from gas chromatographic OTCs, and for many reasons. The HFID [98-102] is a somewhat universal detector for organic compounds. It is also a precise detection device and has excellent response linearity over a broad dynamic range (its response to hydrocarbons is linear over at least five orders of magnitude of solute concentration). Another important property of this detector, especially with respect to HRGC operation, is that its effective dead volume can be very small, approximately a few microliters. With properly designed interior connections, solute zone spreading due to this detector can be extremely small. Highly repeatable data can be obtained with an HFID, provided there is careful adjustment and precise control of the carrier gas, the hydrogen gas flow, the detector auxiliary or supplementary gas, and the flow of compressed air for combustion. Recent experiments have shown [57,103] that increased response is obtained with the HFID if nitrogen is used as the detector auxiliary gas.

If the above variables are adjusted to their optimized values and are precisely controlled, good analytical GC results can be obtained using an HFID in conjunction with a HRGC column. Most of the other detectors used for sensing effluents from OTCs will make a larger contribution to zone spreading as they exhibit small quantities of dead volume associated with their respective detecting mechanisms. As an example, an electron capture detector typically contains a small cylindrical cavity which can introduce a certain amount of zone broadening or detection time lag. The same type of behavior is found for

other devices that have significant internal volumes or chambers associated with their mechanism of detection (e.g., the PID, the HECD, and the UVD). On the contrary, the flame photometric detector, certain mass spectrometric detection devices, and the various bead sensing ionization detectors (e.g., the TSD) have relatively rapid response characteristics. Through the appropriate selection of OTC dimensions and supporting components, the adverse effects of zone broadening from these detectors can be minimized to the point of rivalling the HFID in rapid response characteristics.

Normally, zone broadening contributions at the exit of a chromatographic column are more pronounced when very narrow-bore OTCs or relatively short columns are used for analyzing samples. Conversely, the performance from the longer chromatographic columns, or the wide-bore OTCs, is not affected nearly as much by fixed zone broadening contributions which originate in the column exit region.

3. EFFLUENT SPLITTERS

The use of effluent splitters with capillary columns is a popular procedure [104-107]. In such installations, a chromatographic sample is injected into a single OTC, and the effluent from the column is split into two streams which pass simultaneously into separate detection devices. Much like the series connection of detectors, effluent splitter techniques are very powerful for identifying or classifying compounds of different chemical families [104,107] as the split solute band can be sensed simultaneously with a parallel connection involving a selective detector and a relatively universal detector. Thus, considerable information can be obtained about the chemical nature of a substance. Although effluent splitters have been used for many years with packed columns, an effluent splitter intended for high-performance use with OTCs must be properly designed, carefully constructed, and appropriately installed in the gas chromatographic system.

If the effluent splitter junction (where the column ends and the two detector input transfer lines begin) is at a temperature considerably lower than the detector's, the effluent splitter can cause severe tailing of solutes. As an example, Figure 27 shows a chromatogram of a sample containing a simple mixture of hydrocarbons and a nitrogen-containing species which was sensed using a HFID in parallel with a TSD. Notice the extreme tailing of the emerging solutes. This is a special case in which a short capillary column was temperature programmed at a rapid rate. The severe tailing of the emerging solute was apparently due to two factors. First, the effluent splitter junction was at a temperature much lower (approximately 200°C less) than the bulk temperature of the detectors. Second, there was the probability of stationary phase bleed condensate being deposited in the cool region of the splitter junction. Such pronounced tailing would probably not be observed in situations where a very long OTC or a much slower temperature program rate were being used. For such a case, the temperature difference between the splitter junction and the detector at the time of solute elution would be relatively small. In any event, it seems desirable to have the temperature of the effluent splitter junction and the associated transfer tubing maintained at the same value as the detectors.

4. PLACEMENT OF THE OTC EXIT RELATIVE TO EFFLUENT DETECTION

When a conventional glass OTC is used, the column must have straightened ends so that the column exit is very close to the active region of the detector. There are several problems with installations in which the glass OTC exits some distance from the detector and a transfer tube [108-110] with auxiliary purge has been used for transporting the effluent into the detector. There are difficulties associated with stationary phase bleed from the OTC being deposited nonuniformly in this transfer tube. Also, small crevices in the transfer tube wall [111] tend to introduce asymmetric peak behavior and adsorption.

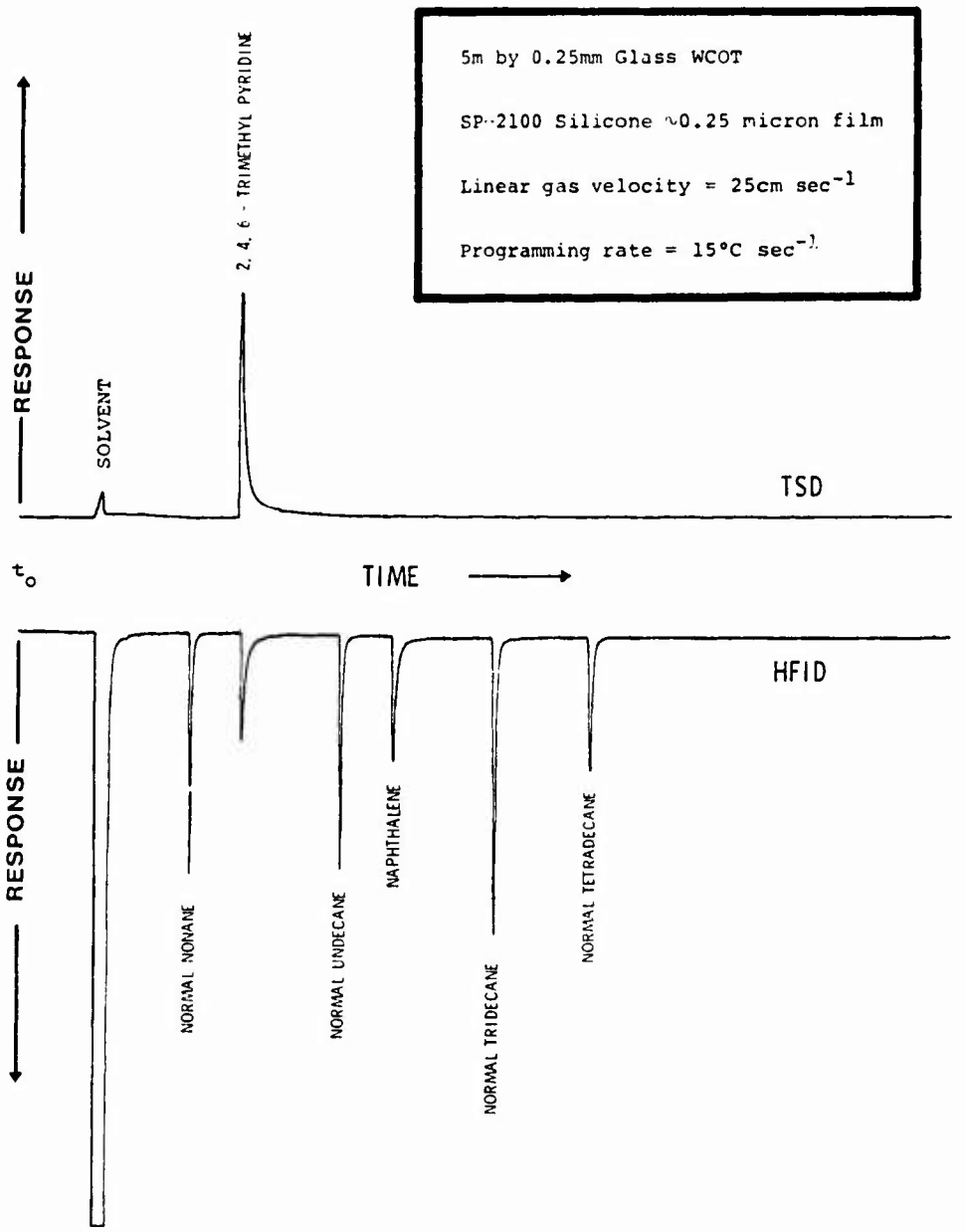


Figure 27. Dual chromatograms obtained with effluent splitter.

With an HFID, attention should be given to precisely maintaining constant flows of the various gases, i.e., the hydrogen fuel, the auxiliary gas, and the air required for combustion. It has been noted that if any of these gas flow rates changes during the course of a GC examination (or from test to test) the detector quantitative response characteristics can change accordingly. When the auxiliary gas flow is interrupted or not used during a GC separation, the HFID response is approximately one-third that normally encountered with an optimized flow of auxiliary gas.

Excessive HFID temperature can present several problems. These can be minimized if the detector temperature is adjusted to a value just slightly higher than the maximum temperature in a programmed GC test, or if the detector is set at the same temperature at which the OTC was conditioned.

Earlier in this section, a certain HFID design [97] as presented by Gaspar, et al. was discussed. Also, a sketch was presented (see Figure 26) of a modified HFID and adaptor assembly used in our laboratory studies. If a HFID assembly for HRGC has been properly designed, attention has gone into minimizing any zone spreading associated with effluent detection. This is usually accomplished by designing the detector cell for the smallest possible interior volume or by designing for a very rapid transit time from the column exit to the active region of the detection device. Special attention must also go to the composition, design, and location of a HFID's electrodes and to the geometry of the flame-tip. Before discussing these HFID design aspects further, it would be appropriate to address other potential problems associated with the HFID.

A properly adjusted HFID should have a stable flame and low signal noise, which minimize signal transients and cyclic distortions. The various gas flows are important in this regard and the detector auxiliary gas flow is especially critical. As stated earlier, nitrogen is the preferred auxiliary gas as it produces a larger HFID response. However, to obtain a stable

low-noise flame, the detector gases must be carefully purified and the effluent emerging from the OTC must be thoroughly mixed before the composite gas stream enters the actual flame. The quality of the quantitative data is dependent upon the minimization of short-term noise.

The diameter of the opening in the HFID flame-tip must be large enough that only a negligible pressure drop occurs across this jet. If a significant or varying pressure difference occurs across this opening, it could affect the actual retention behavior of emerging solute zones. Conversely, the flame-tip aperture should be small enough to act as an orifice and permit mixing of the OTC effluent, the auxiliary gas, and the hydrogen prior to entering the flame. This orifice serves as a boundary between the regions where the mixed gases rapidly sweep the OTC exit and the onset of the diffusion-controlled flame.

In Section VI, some of the adverse behavior that can occur because of a dirty HFID flame-tip was discussed. It has been stated recently that a dirty flame-tip can be a major cause of peak tailing [67] for organic compounds that contain bound nitrogen, thus stressing that serious consideration should be given to the flame-tip assembly of a HFID.

The materials selected for the interior of a HFID assembly and the way they are used are important. Ceramics can be excellent electrical insulators, although many ceramics also tend to be adsorptive and some are even porous; certain hot metal surfaces can be catalytically active and adsorptive. A HFID insert assembly used in our laboratory studies is shown by sketch in Figure 28. The design of this detector insert assembly incorporates a sleeve guide for concentrically aligning the flexible fused silica OTC which terminates at a precise location near the flame-tip aperture. This design also preheats the auxiliary gas and the hydrogen prior to mixing with the OTC effluent near the HFID aperture. The final positioning of the stainless steel alignment guide and the fused silica OTC is detailed in Figure 29.

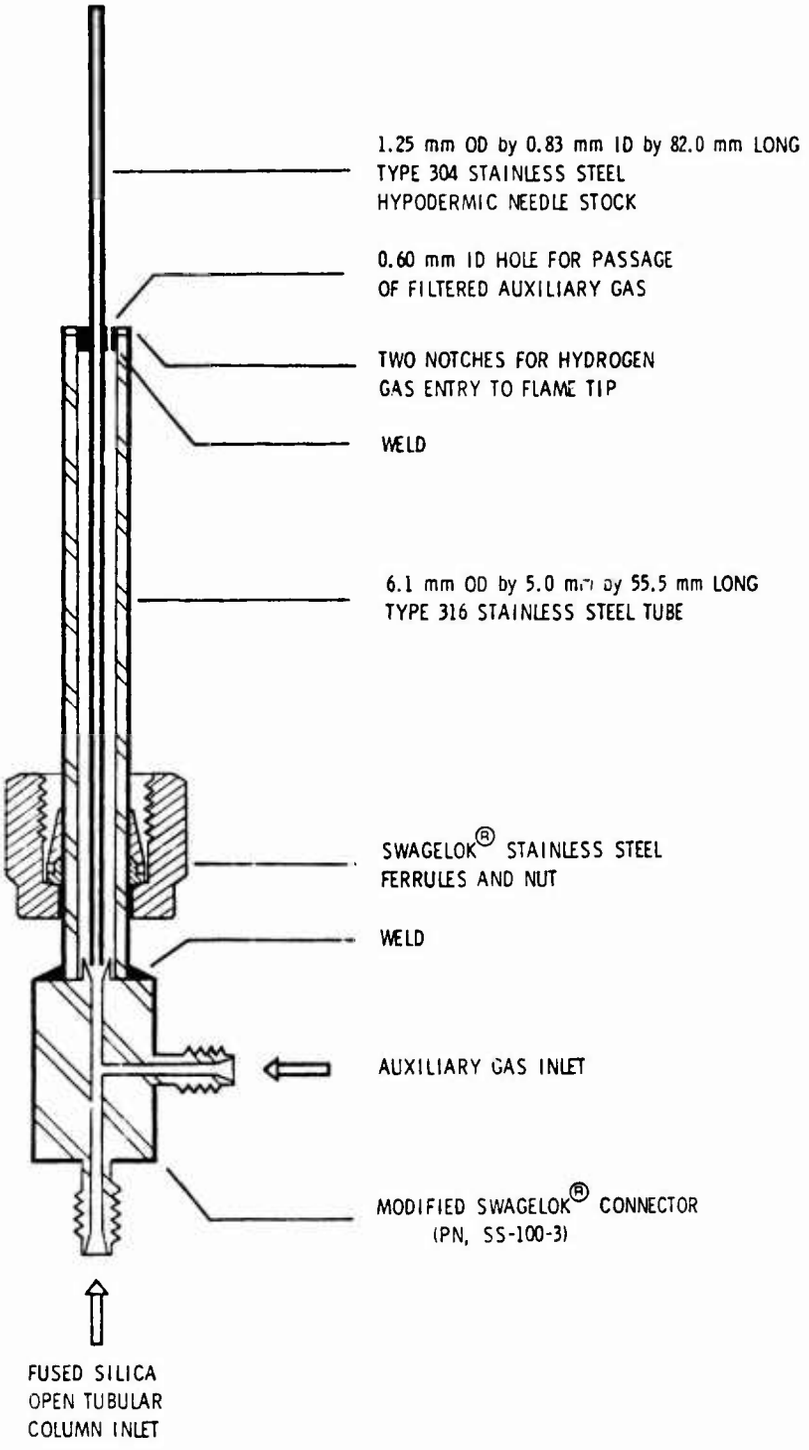


Figure 28. A special insert adapter assembly for an open tubular column in a hydrogen flame ionization detector.

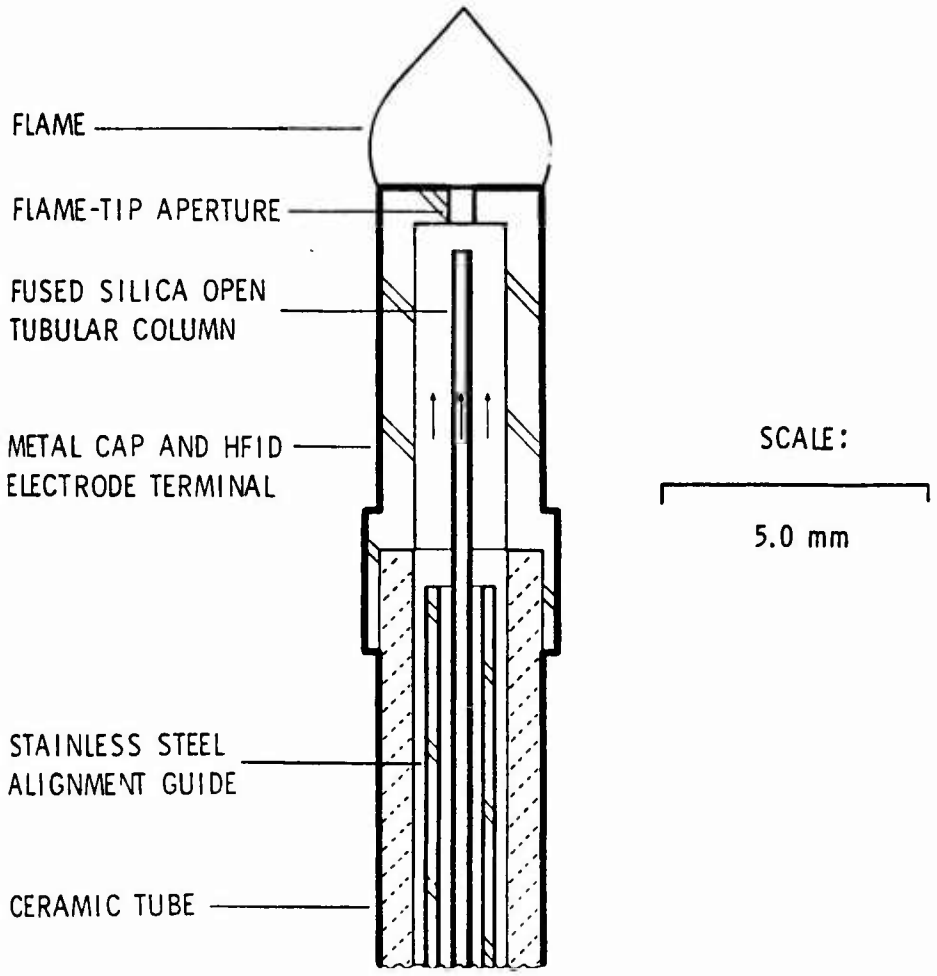


Figure 29. Detail of alignment guide and the open tubular column.

When an OTC is first installed in this detector assembly, the fused silica OTC is passed through the flame-tip opening and allowed to extend beyond the upper surface of the flame-tip by approximately 1.5 millimeters. The column is then conditioned with the OTC exit located as shown in Figure 30a. After the OTC has been conditioned, the flame is ignited and the extended portion of the polyimide outer coating is burned away. The fused silica column is then retracted to the lower position as shown in Figure 30b. Notice that the conditioned fused silica OTC is concentrically located in this assembly through the use of the stainless steel sleeve guide. During subsequent analytical work the OTC exit is maintained at this lower position. This procedure for conditioning the column and later burning away a small portion of the polyimide outer coating decreases the possibility of responding substances liberated from the exit portion of the tubing passing into the flame and causing disturbances, e.g., spurious electrical transients, elevated or cyclic baseline, etc.

There are several reasons for giving so much attention to the OTC exit location relative to its termination in the HFID. If the OTC exit were permitted to remain in the flame-tip orifice, it would continually vibrate in the high-velocity flow of sweeping gas. Such an installation would probably produce varying pressure conditions upstream of the aperture which could affect GC retention behavior. Even with an enlarged aperture, the continual vibration of the coated fused silica tube against the aperture wall would tend to degrade the polyimide outer coating and cause spurious transients as a result of the abrasive conditions. Furthermore, if the end of the OTC was lying either to one side of the flame-tip cavity or butted against the lower surface of the flame-tip as shown in Figures 31a and 31b, the resultant gas sweeping and instantaneous mixing action would not be as desired. If residual levels of stationary phase were to migrate into these recesses, selective sorption and peak tailing could result.

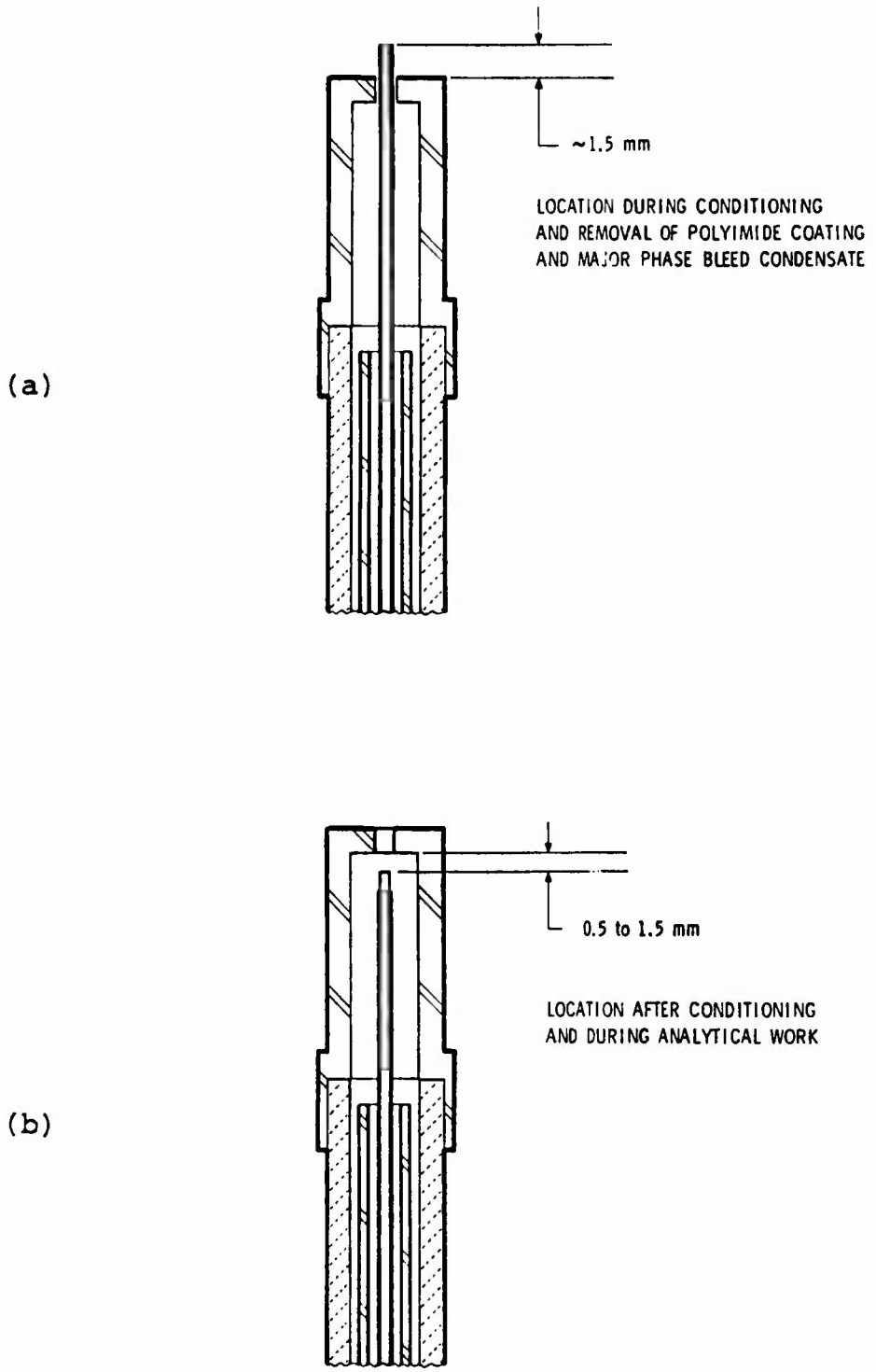


Figure 30. Open tubular column positioning.

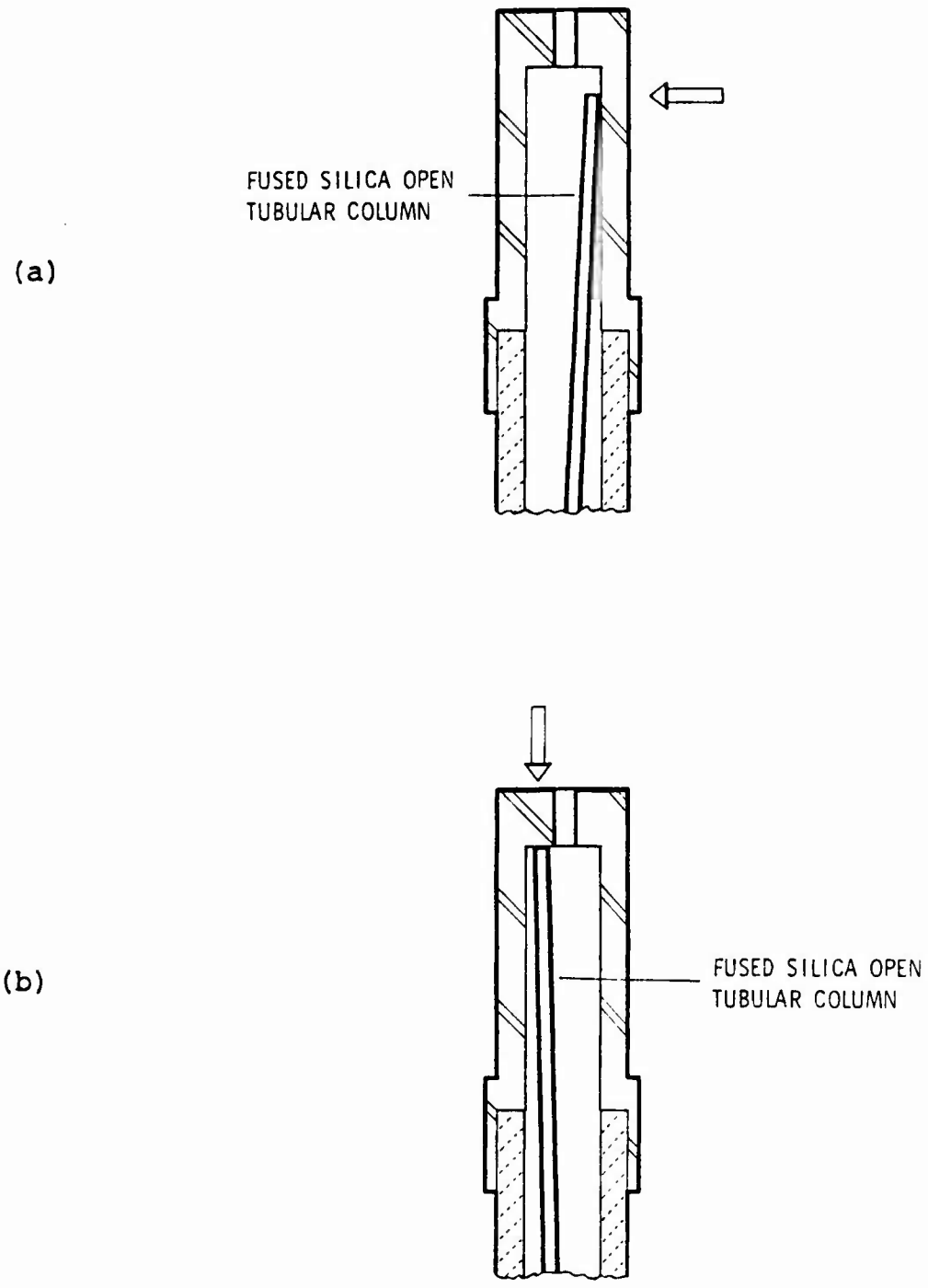


Figure 31. Undesirable exit locations for the open tubular column.

The behavior of this OTC exit-HFID assembly has been most satisfactory. At no time have distorted pure hydrocarbon solute zones been observed, such as those shown in Figure 24. This assembly has permitted us to observe emerging recorded solute zones and to make assessments with respect to superimposed and partially disengaged solute species. The emerging low-concentration solutes are well behaved and are eluted with symmetrical zone profiles. In addition, transient spiking has been minimized and long-term noise (e.g., excessive baseline drift and cycling) has not been observed. With this preconditioned flame-tip assembly, bleed from the column is minimized and the existing residual level of stationary phase bleed invariably observed during temperature programming to the higher temperatures is consistently repeatable.

SECTION VIII

TREATMENT OF OUPUT SIGNAL AND PROCESSING OF HIGH-RESOLUTION GAS CHROMATOGRAPHIC DATA

For maximum available information to be obtained from a high-resolution gas chromatographic system, the output signal must be appropriately amplified and recorded, and considerable attention must be given to the presentation and graphic display of chromatograms. Storage of the raw HRGC data and its eventual analysis also require special treatment.

1. ACCURATE MEASUREMENT AND RECORDING OF OUTPUT SIGNAL

The analog output signal from a typical gas chromatograph is somewhat noisy and subject to short-term drift [112]. This low-level direct-current signal normally encounters some degree of filtration by the various signal handling devices, i.e., the electrometer amplifier, the electronic integrator, the potentiometric recorder, etc. For a better grasp of these typical GC signals, electrical measurements were taken from a Varian 1800 gas chromatograph. These signal tracings are shown in Figures 32 to 35.

The electrometer output signal is depicted by the oscilloscope trace presented in Figure 32. This signal is evidently noisy, yet the bursts seem to be periodic. Figure 33 shows the filtered chromatographic signal at the output of the electronic integrator or at the input to the recorder, and Figure 34 is the potentiometric recorder output tracing showing the short-term drift corresponding to the most sensitive electrometer setting on the chromatograph. Figure 35 illustrates the GC signal encountered at the more commonly used ouput presentation level of 8×10^{-12} amperes full scale.

The faithful recording of the concentration of emerging solutes from a HRGC instrument requires an electrometer amplifier with a rapid response time [113]. If the electrometer amplifier cannot follow the signal from the detector, there will be a time

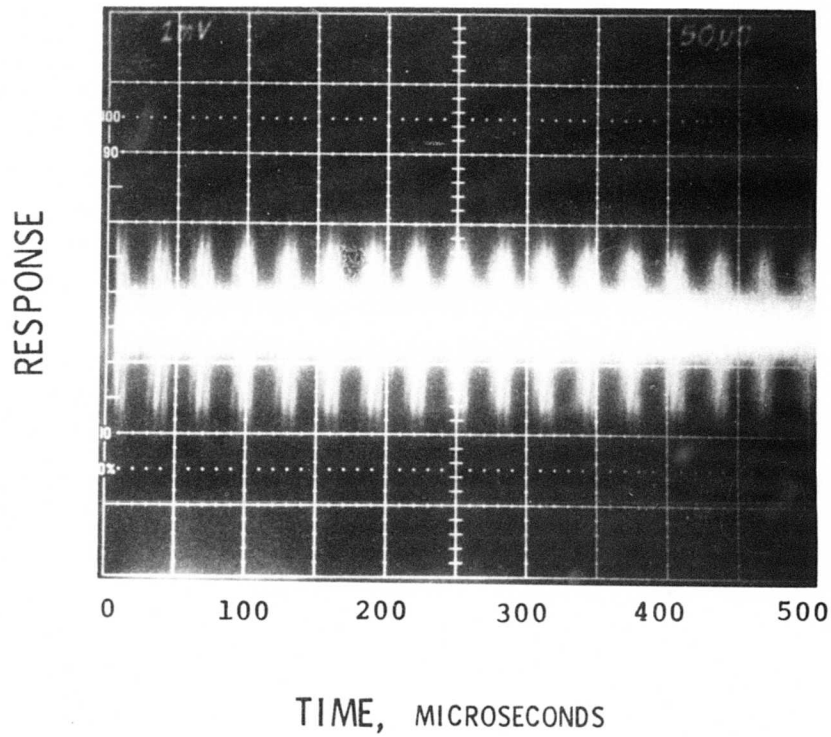


Figure 32. Oscilloscope trace of electrometer output.

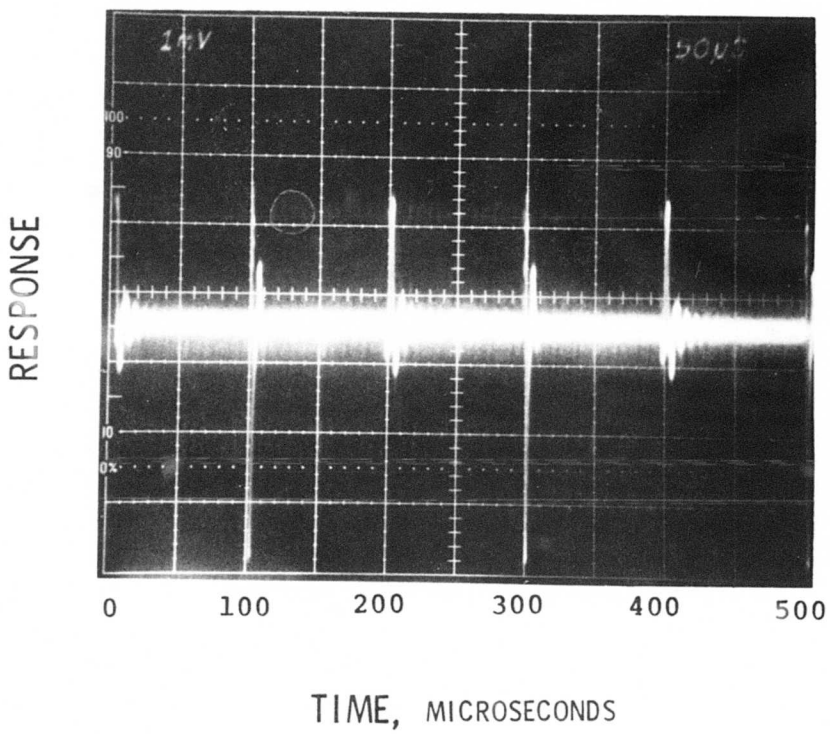


Figure 33. Oscilloscope trace at integrator output.

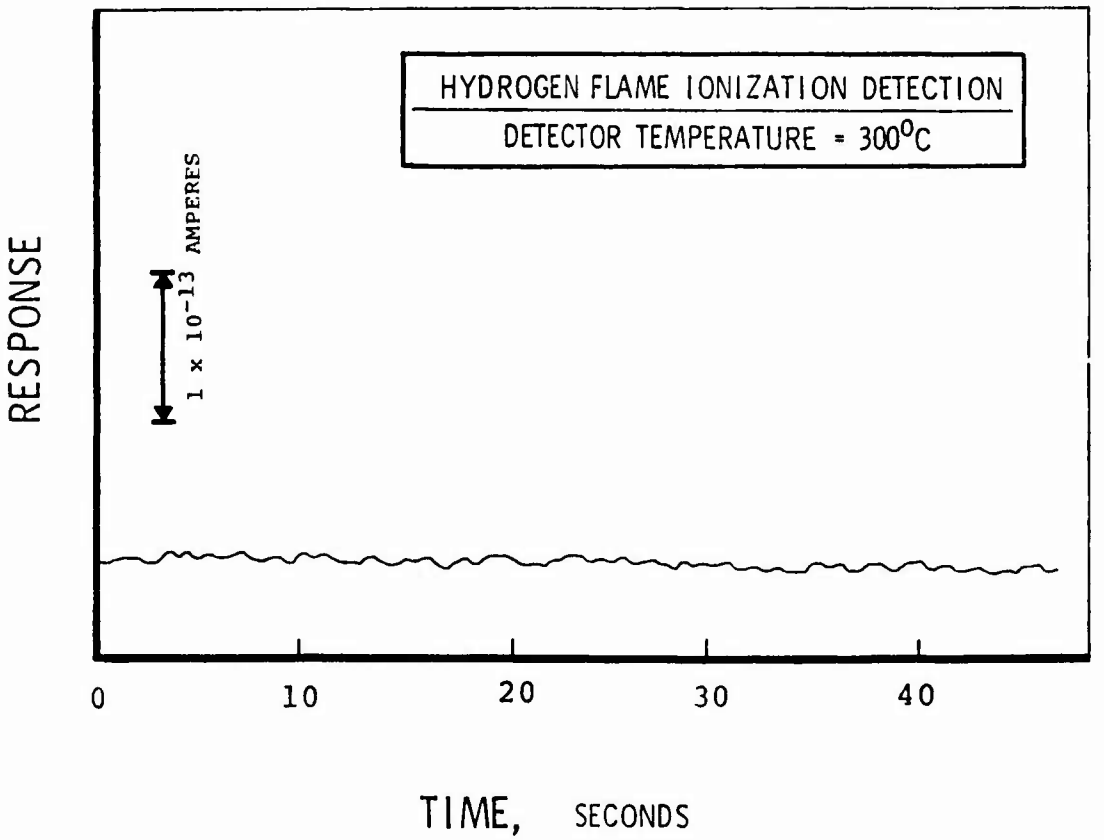


Figure 34. Potentiometric recorder output tracing under most sensitive setting.

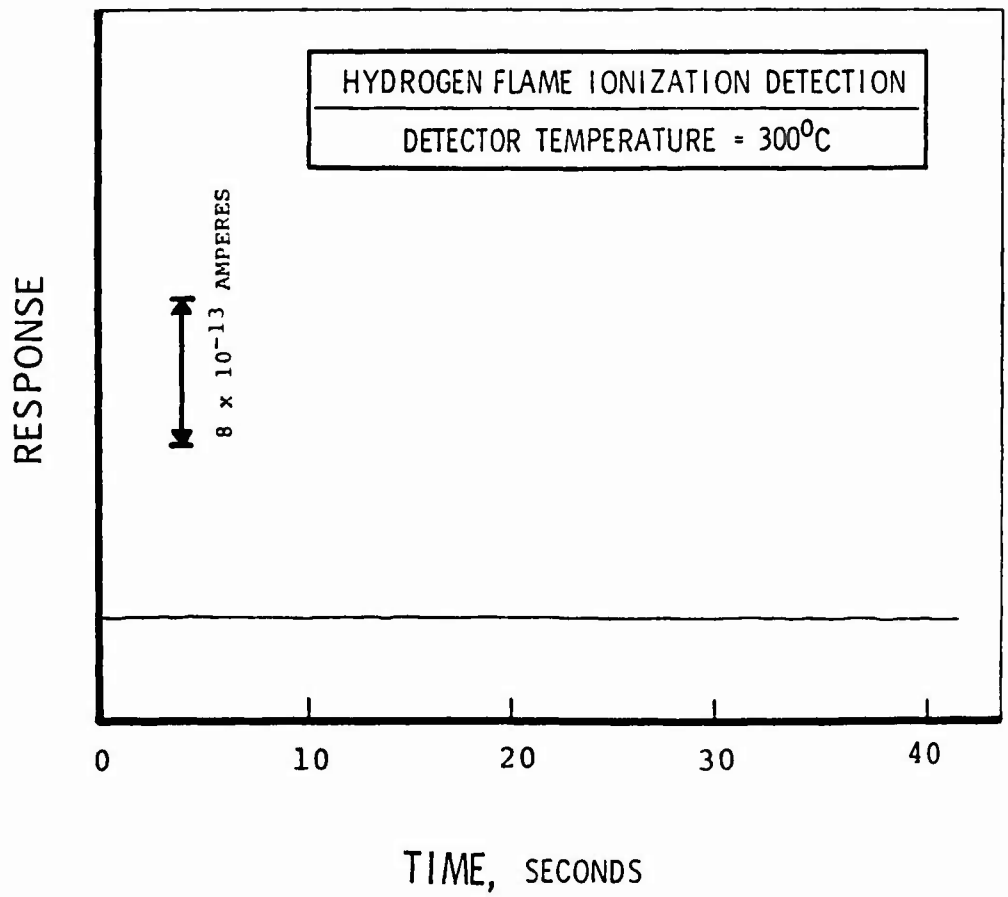


Figure 35. Recorder signal at common typical electrometer attenuation.

lag in the output voltage versus time relationship. Some GC profile information will be lost. Slow electrometer response will affect such factors as (a) the height of a rapidly emerging solute zone, (b) the width of a GC peak (thereby the calculated chromatographic efficiency), (c) the resolution of adjacent solute zones, (d) the retention data (as the centroid of an emerging profile would be shifted to some later time) and, (e) profile symmetry.

The electrometer time constant can be changed in some recently designed chromatographic instruments. In some cases this requires a simple circuit modification to obtain approximately a 100-millisecond time constant. The need for fast electrometers has been recognized and the instrument manufacturers are addressing this need.

2. CHROMATOGRAPHIC RECORDER REQUIREMENTS

The device for recording the output signal is especially important in HRGC. This device must possess a rapid response time and exhibit a linear response to GC input signals. The recorder response time can be determined by using a low-frequency signal generator and measuring the cyclic response of the device. The response linearity can be established with a decade step voltage standard.

The degree of isolation of the recorder should also be checked periodically. Specifically, it is important to determine if the HRGC recording system is affected by stray external signals or fields, as this could increase the background level and even the quantitations associated with some chromatographic tracings. A good graphic recording system should have the ability to adjust the gain and damping of the recorder so it is slightly under-damped, thereby obtaining a recording pen that is "live". Having a "live" recorder pen ensures there is not lost motion or finite dead band occurring in the output potentiometric tracing.

In HRGC, the chromatographer must rely considerably upon the actual shape of the emerging GC solute profile. This is a major diagnostic tool, particularly if the analyst wants to determine if he has more than one substance eluting under a particular chromatographic profile. For this type of diagnostic investigation, the signal recording equipment must be especially faithful in its response. In addition, this signal recording equipment should be uniform and constant in its chart advance rate. The chart movement must be continuous, that is, it must not have an irregular, intermittent, jerky motion. Most recorders contain either a synchronous drive mechanism or a rapid stepper motor for chart advance; however, the paper advance itself is the most important characteristic.

Sprocket chart drive recorders and potentiometric recorders that use a belt drive tend to produce an irregular intermittent chart motion. In the graphic recording of a signal that is evenly changing, this intermittent chart advance can be observed as a "stair-stepping" type of signal display. Slow intermittent step recording of the signal, as opposed to the correct smooth recording of the voltage versus time function, presents severe difficulties in visibly detecting the presence of merged solute zones superimposed under one major emerging profile. Potentiometric recorders exhibiting smooth chart advances, such as the friction or roller drive chart advance mechanisms, produce a recorded trace that assists in the discernment of overlapping elution species.

For accurately recording high-resolution chromatograms obtained using rapid separation gas chromatographic techniques, advanced oscillographic recorders or digital computer techniques would probably be necessary for recording chromatographic profiles. Oscillographic recorders now available can record extremely narrow signal profiles (approximately 0.5 millisecond duration) and produce a permanent graphic record.

For very high-efficiency OTC gas chromatography, the fidelity of the analytical signal generation and recording system must be ensured. In short, the detection, amplification, and read-out system must present a faithful response, especially when dealing with complex chromatograms, such as those produced by hydrocarbon fuels, where there are numerous partially resolved solute zones.

3. DISPLAY OF OTC GAS CHROMATOGRAMS

As HRGC advances into the megaplate region ($n \geq 1 \times 10^6$) a real problem exists in storing and displaying the chromatographic signal tracings. Figure 36 shows nine partial tracings which constitute one complete chromatogram. The attempt here was to place the entire recorded GC output signal on a single sheet of 8 1/2"-by-11" paper so that the chromatogram of the sample could be observed in the usual manner without leafing from page to page. Indeed, this is a problem of graphic reproduction and storage of data.

Today it is very difficult to present a HRGC chromatogram on one sheet of paper such as would appear in a technical report or journal article. If the chromatogram has been photographically reduced, the line widths are usually so narrow that they cannot be reproduced, and if wider line widths were used for the original graphic recording of chromatograms, much information would be lost, as several peaks can be obliterated by the width of the recording pen or stylus. It is relatively common today to see in journals, HRGC chromatograms that exhibit faint broken lines and which, in short, do not represent a clear record of the voltage versus time profiles, i.e., the chromatogram. Although certain important areas of the chromatogram can be photographically enlarged and presented with clarity, there remains a real problem in displaying the full information content that can be generated by a HRGC instrument.

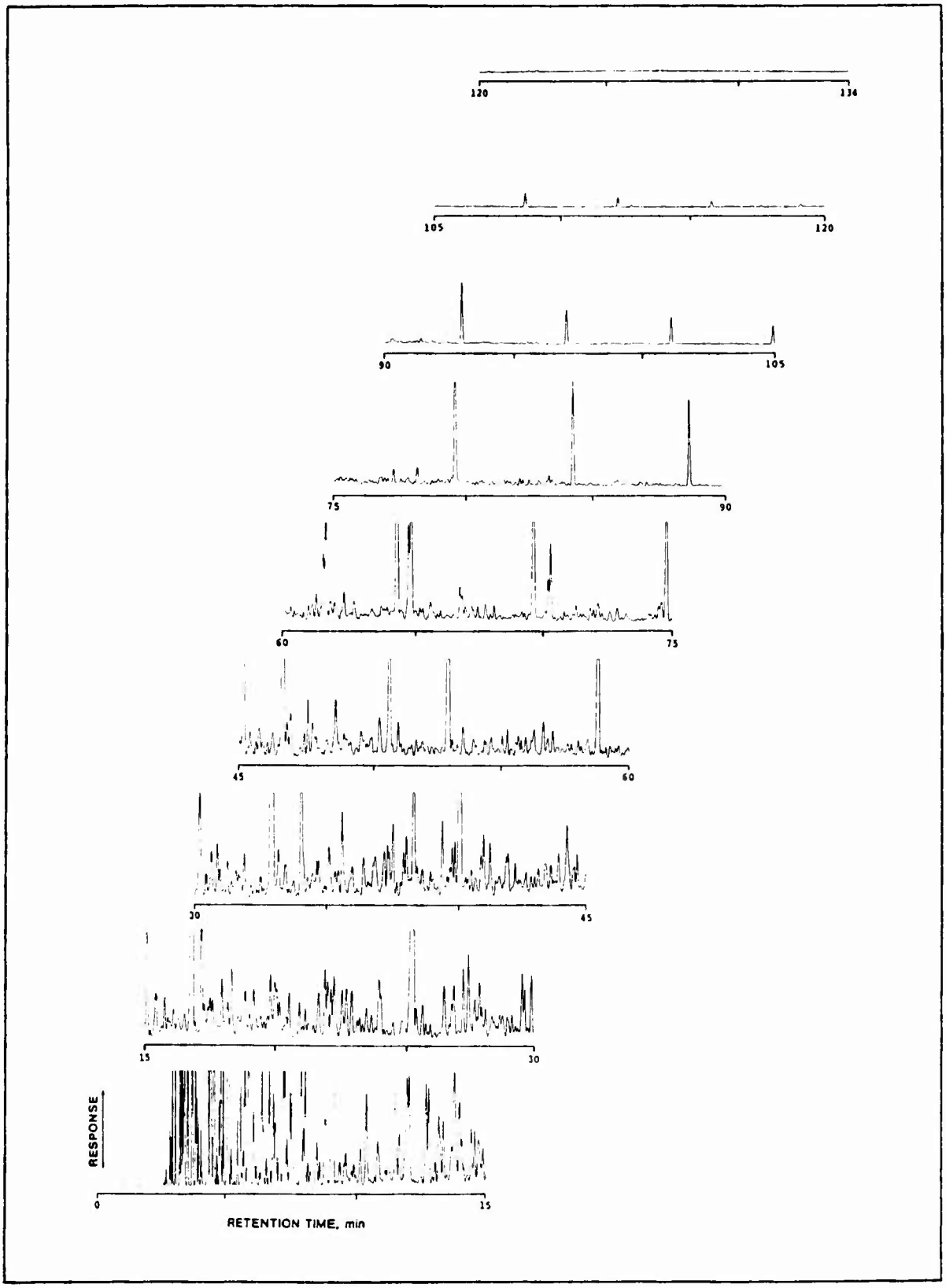


Figure 36. Nine partial tracings which constitute one complete complex chromatogram.

A graphic presentation technique that may see renewed interest is actually using a log-scale ordinate display for the chromatographic signal [114]. This method of displaying the raw chromatographic output signal permits improved detection of trace-level components while it keeps the large solute concentrations on-scale. Logarithmic recording can be accomplished with potentiometric recorders and oscillographic recorders. This log-response feature is incorporated into many digital integrating devices.

Another interesting approach is the recording of chromatograms in a circular display [115]. The conventional strip chart Cartesian coordinates need not be the only format for presenting HRGC data. Circular chromatographic tracings can also be generated in the log-response mode.

One valuable technique for presenting HRGC data is producing a dual tracing of the same GC output signal. Figure 37 shows a dual tracing where the signal is applied to both inputs of a dual channel potentiometric recorder. The amplification for one channel is adjusted for a 1.0 millivolt full-scale representation, while the other channel is adjusted for a 100-millivolt full-scale setting. This permits the large solute peaks to be displayed on-scale on the low-sensitivity channel, and as the larger solute zones are driven off-scale on the sensitive channel, the very small solute concentrations are amply displayed. Such an output signal recording scheme permits ready examination of the major and the minor constituents of a sample mixture.

4. STORAGE OF CHROMATOGRAPHIC DATA

A powerful and elegant method for processing HRGC data is recording the entire GC output signal with the use of a dedicated computer [116-118]. Then at some later time, the particular chromatographic data are regenerated through playback. The GC signals can then be graphically recorded in any of several modes.

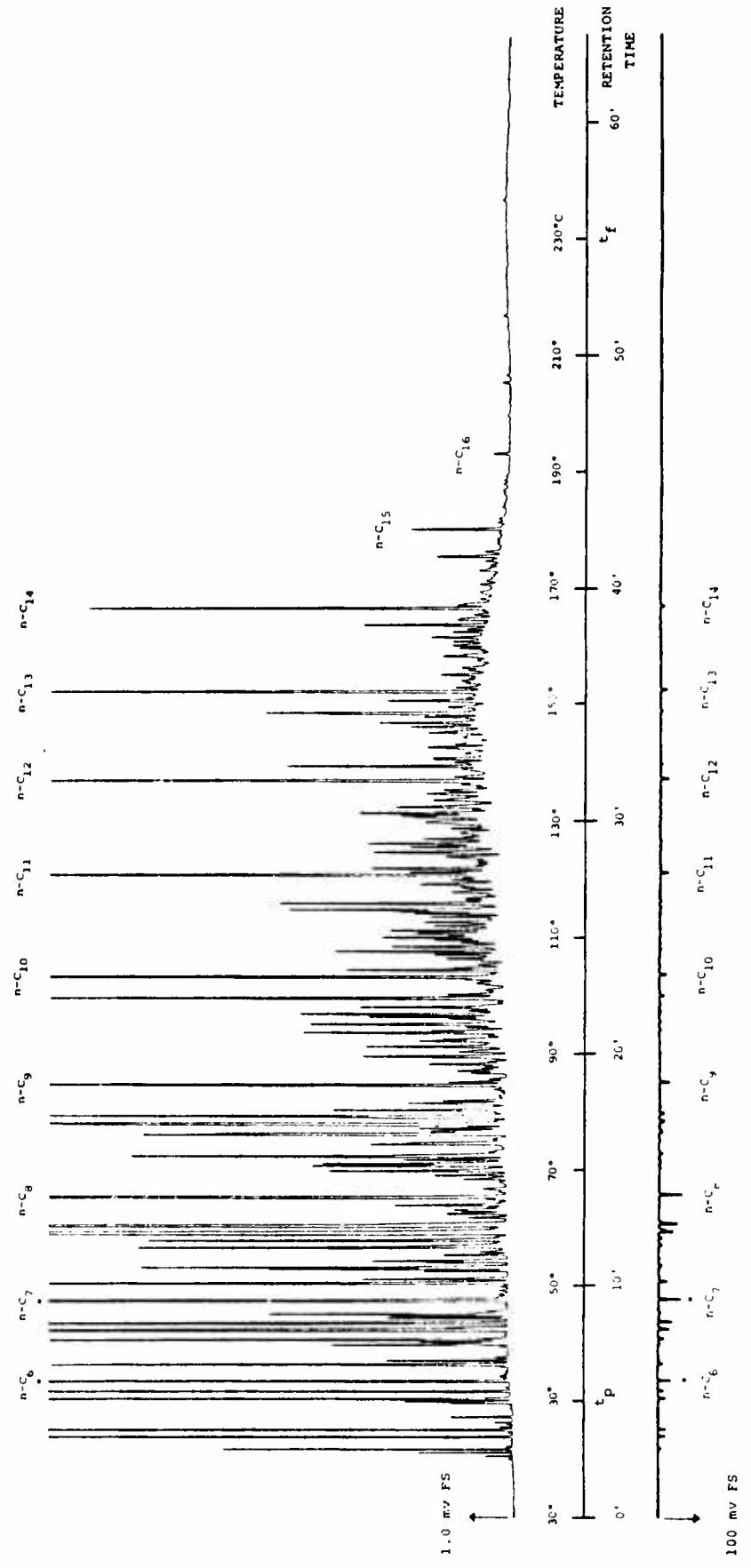


Figure 37. Dual chromatographic tracing at sensitivities that differ by a factor of 100.

With this method, the time base can be expanded so that a detailed examination can be made of those select regions of the chromatograms which are of high interest. The time base can be condensed so that the entire tracing can be reproduced on a single sheet of paper.

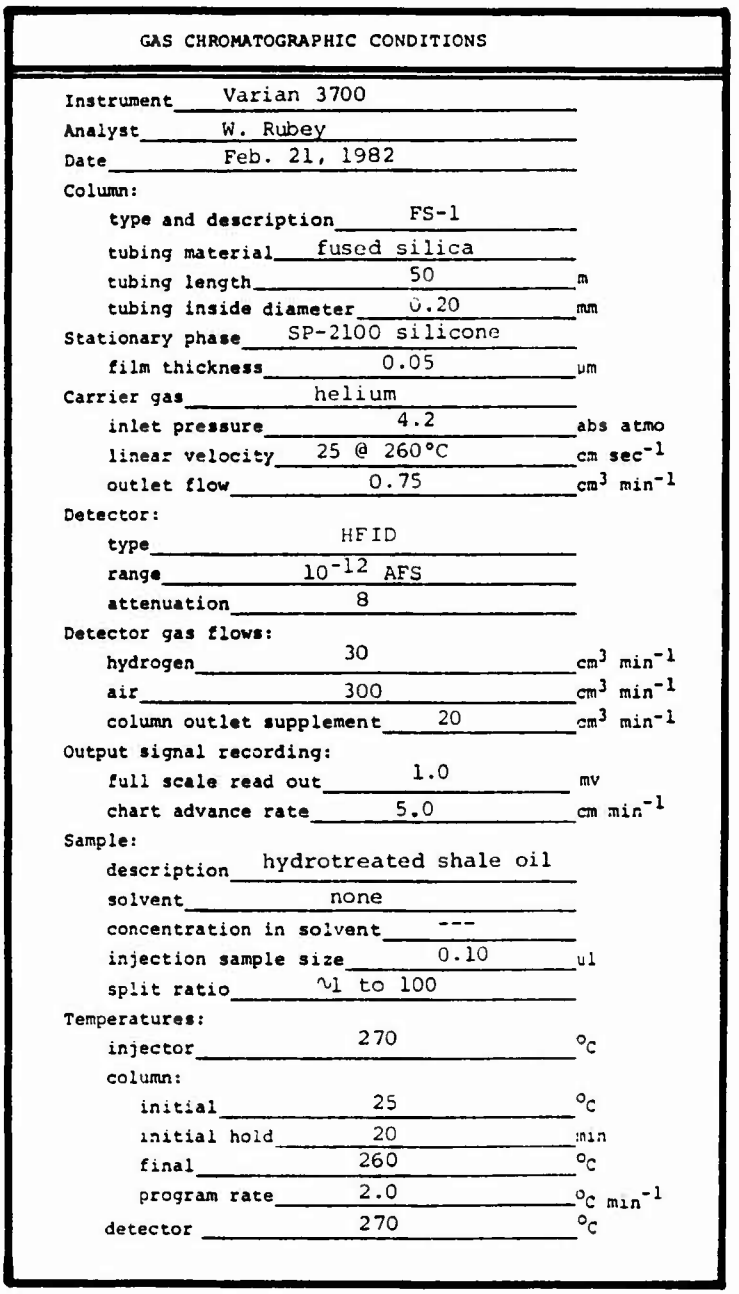
Since the raw GC data are stored on tape or disk, it is possible to go back later and look at any portion of the GC tracing in detail. Through an exacting examination of each of the various recorded elution profiles, the detection of merged solute zones [119-121] should be possible. Of course, by having the raw HRGC data in storage, numerous computer processing and data handling techniques could be applied at any time in the future.

5. ANALYSIS OF CHROMATOGRAPHIC DATA

The total chromatogram as shown in Figure 36 represented the output signal tracing for a sample that contained at least 1,154 different chemical compounds. The chromatogram was obtained under the conditions defined in Figure 38 and the solutes were counted as they emerged, using a hand counter.

The presence of different solute zones can be observed by (a) an individual peak cresting, (b) a shoulder, (c) an inflection, (d) a flattening in a certain region of the profile, and (e) any distortion to the basic Gaussian solute concentration. The particular research grade gas chromatograph used for generating this HRGC chromatogram was capable of generating solute profiles that conformed very closely to the ideal Gaussian function.

One of the major objectives in HRGC is to separate the various constituents of a mixture so that accurate quantitations can be made and appropriate data obtained for the various solutes. There are basically two procedures currently used for measuring the solute zone and obtaining quantitative information on the constituents that make up the entire sample. The height of the recorded solute zone (commonly referred to as peak height) is one measurement parameter and the integrated response (peak area) is



GAS CHROMATOGRAPHIC CONDITIONS

Instrument: Varian 3700
Analyst: W. Rubey
Date: Feb. 21, 1982
Column:
- type and description: FS-1
- tubing material: fused silica
- tubing length: 50 m
- tubing inside diameter: 0.20 mm

Stationary phase: SP-2100 silicone
- film thickness: 0.05 um

Carrier gas: helium
- inlet pressure: 4.2 abs atmo
- linear velocity: 25 @ 260°C cm sec^{-1}
- outlet flow: 0.75 cm^3 min^{-1}

Detector:
- type: HFID
- range: 10^{-12} AFS
- attenuation: 8

Detector gas flows:
- hydrogen: 30 cm^3 min^{-1}
- air: 300 cm^3 min^{-1}
- column outlet supplement: 20 cm^3 min^{-1}

Output signal recording:
- full scale read out: 1.0 mv
- chart advance rate: 5.0 cm min^{-1}

Sample:
- description: hydrotreated shale oil
- solvent: none
- concentration in solvent: ---
- injection sample size: 0.10 ul
- split ratio: ~1 to 100

Temperatures:
- injector: 270 °C
- column:
  - initial: 25 °C
  - initial hold: 20 min
  - final: 260 °C
  - program rate: 2.0 °C min^{-1}
- detector: 270 °C

Figure 38. Conditions for complex sample chromatogram shown in Figure 36.

the other. Instrumentation and measurement procedures for determining peak area are widely used [17,122]. Although area measurement techniques are the most common method for obtaining basic quantitative data from recorded chromatographic data, in certain situations peak height data are of value [94,123,124] and even preferred.

With either of these two measurement procedures, it is apparent that the quality of the eventual data is dependent upon the extent of solute zone disengagement, i.e., the resolution that exists for the various solute zones. The same situation applies to qualitative analysis. If the solute zones are sufficiently separated, precise retention data can be obtained.

Jet fuels, crude oils, and shale oils contain a wide range of organic substances and, as discussed previously, definitely require programmed temperature GC procedures [125] for separation of the numerous constituents. The Kovats retention index [126] was originally developed as a standard method of characterizing solute retention behavior in isothermal GC. The Kovats index method has also been applied in programmed temperature GC chromatography [127] and it is now the preferred technique for obtaining strictly chromatographic qualitative data for hydrocarbon fuels.

The gas chromatographic stationary phases that seem most appropriate for characterizing jet fuels relative to retention data are currently undergoing some revisions. Specifically, there seems to be a trend toward the chemically bonded stationary phases in OTC technology. If these chemically bonded phases perform as expected, the bonded equivalent dimethyl silicone, 5% phenyl methyl silicone, 20% phenyl methyl silicone, and 50% phenyl methyl silicone stationary phases would seem to be the most acceptable for analyzing and obtaining Kovats retention data for hydrocarbon turbine engine fuels.

SECTION IX

TRENDS IN HIGH-RESOLUTION GAS CHROMATOGRAPHY AS RELATED TO FUTURE ANALYSIS OF HYDROCARBON FUELS

Aviation turbine fuels will continue to be analyzed by chromatography in the future and for such complex hydrocarbon mixtures high-resolution gas chromatography will be the major technique. This analytical technique is experiencing widespread growth, and research involving various aspects of HRGC is quite active. Certainly the most immediate problem to be addressed relative to advancing the HRGC analysis of hydrocarbon fuels is development of automated and appropriate sample insertion techniques. Fortunately, intense research is ongoing in this particular area.

1. GENERAL FUTURE TRENDS AND THEORETICAL CONSIDERATIONS

Before discussing some of the newly emerging chromatographic procedures that may be applied to the analysis of hydrocarbon fuels, it would be appropriate to consider some of the recent theoretical studies concerning the ultimate potentials of various chromatographic separation techniques [128-132]. These studies put forth and discuss upper limits for chromatographic efficiency and speed of analysis. The predictions are founded upon the physio-chemical principles that govern the basic chromatographic processs. The theoretical and practical ranges of OTC gas chromatography were recently investigated by Yang, et al. [128]. Also, an unusual approach to the theoretical limitations of OTC performance was recently put forth [129]. The future pathways for analytical separations and various fundamental approaches to resolving solutes have recently been studied by Giddings [130,131]. In addition Guiochon [132] has conducted theoretical studies on the ultimate speeds of separation for both gas and liquid chromatography.

The limitations of noncircular cross-section OTCs have recently been studied [133,134], and conclusions have been drawn

concerning the behavior of different geometrical flowpaths. The future of multimember OTC systems remains to be the subject of considerable discussion, and the use of chromatographic systems is definitely one promising direction for obtaining increased performance in HRGC [135]. Special versions of the various "hyphenated methods"[136] are also applicable to the analysis of hydrocarbon fuels.

Several newly emerging instrumental techniques may someday be applied to the analysis of hydrocarbon mixtures. OTC zone electrophoresis [137] and multiplex gas chromatography [138] may find application in separating the constituents of complex samples. There is also considerable interest in capillary supercritical fluid chromatography [139-143], and several investigations have been reported in this emerging technological area.

2. APPLICATION AREAS RECEIVING ATTENTION WITH RESPECT TO INCREASED ANALYTICAL CAPABILITIES

The chromatographic needs for the industrial petrochemical laboratory were recently reviewed [144], as were the problems and solutions associated with commercially available chromatographic instrumentation [145] and the chromatographic needs involved in analyzing environmental samples [146].

Considerable attention has been given to the development of an OTC stationary phase that would be suitable for resolving the four basic hydrocarbon fuel groups, e.g., paraffins, olefins, naphthenes, and aromatics [147]. Accordingly, a 20% phenylmethylsilicone OTC has evolved which efficiently handles these classes of compounds. Attention continues to be focused upon the selectivity of chemically bonded stationary phases, and only recently thick film (1.0 microns) and very thick film (8.0 microns) OTCs have been prepared and evaluated [148,149].

With respect to shale oils and coal liquids, improved procedures are being developed for analyzing the light oil alkanes in shale oil [150] and sulfur heterocycles in coal

liquids and shale oils [151]. HRGC is also being applied to the analysis of coal-derived liquids [152].

There is increased interest in being able to rapidly analyze for the highly volatile organic constituents in complex mixtures [153]. Routine analyses for volatile components in such mixtures are being developed, and improved procedures are being employed using head-space OTC gas chromatography [154]. With respect to complex hydrocarbon feedstocks, current investigation involves chromatographic subtraction techniques wherein certain classes of compounds are selectively subtracted from the complex sample matrix prior to its introduction into a HRGC system. Proper use of these subtraction techniques can dramatically simplify analyses, as in many cases the chromatographic solutes of interest may be viewed without interfering solute zones. These subtraction techniques can be used with existing equipment and usually these procedures are relatively simple. However, the analyst must be continually aware that he is analyzing a preprocessed sample and not the total intact sample. The use of subtraction techniques whereby the naphthene fraction has been removed from a hydrocarbon fuel generally yields a much better behaved HRGC baseline for the region corresponding to the C_{10} to C_{16} hydrocarbons.

Fractionation or preseparation techniques have been used to advantage with wastewater samples [155] and very complex organic mixtures such as polynuclear aromatic hydrocarbons. Chemical class separation and characterization techniques have recently been developed for organic compounds in synfuels [156]. Chromatographic preseparation procedures have also been applied for conventional and experimental fuels [157]. Analytical techniques, where one class of compounds is subtracted from the entire sample and only the passable substances are transported on to the detection device, have been used for many years [158]. Other subtraction methods which simplify the fuel sample have been employed in subtraction gas chromatographic techniques [159].

There is renewed interest in high-efficiency preparative collection techniques [160] and some progress is being made in this area. There has also been some preparative work conducted with glass OTCs where many sample injections are made, but only a select fraction, or group of compounds, is repetitively collected for subsequent analysis [161]. It was recently found, with the bonded-phase OTCs, that very large samples could be injected into the column, thereby permitting trace level analyses of some solutes to be performed in this highly overloaded condition [162].

Analytical interest in the various geochemical feedstocks is intense. Accordingly, HRGC is finding increased application in this area. This trend will undoubtedly continue into the future. Procedures to analyze for pristane, phytane, squalane, and various isoprenoid hydrocarbons in petroleum synfuel feedstocks and organic waxes are being developed [163-169]. Elucidation of geomatrices by laser pyrolysis-gas chromatography has recently been undertaken [170], and gas chromatographic-mass spectrometric identification has been applied to various geochemically significant isoalkane hydrocarbons [164].

3. GAS CHROMATOGRAPHIC COLUMN RESEARCH

Interest continues in novel chromatographic columns having different geometric configurations. Several new column forms have been considered for HRGC [171,172], and one of the major objectives in these efforts has been to obtain columns that exhibit a flat $\hat{H}$ versus velocity curve at the higher mobile phase velocities. In short, if a chromatographic column possessed an optimum linear gas velocity of approximately a meter per second while at the same time it was still an efficient column, then it would be possible to generate HRGC data in a very short time.

Inducing secondary flow in chromatographic columns has been investigated [173,174]. Theoretical treatments indicate that there is some potential in this area. However, in practice it is difficult to establish this type of flow in realistic columns, although several attempts have been made. The work carried out

thus far with secondary flow has used uncoated tubes. With the recent advent of bonded-phase OTCs, this topic warrants further investigation.

The need for higher resolution and increased column efficiency in HRGC is apparent when one analyzes a very complex natural occurring organic sample, e.g., a petroleum crude sample or a synfuel feedstock. Inevitably, even with some of the best columns, there is a hump in the middle of the chromatogram where the baseline is elevated due to the superposition of many unresolved sample constituents [175]. As the efficiency and resolution of a particular chromatographic system increase, this baseline hump diminishes. Work with some of the recent microbore OTCs (30 to 140 micron inside diameter) has shown a marked decrease in this hump; however, these columns can only accept a very small amount of sample and they produce a significant pressure drop.

Theoretical studies [176] of peak capacity and resolution have attempted to answer basic questions as to whether we are obtaining the full resolving power of our columns [177]. Also, further studies of the working range [178] of HRGC columns would seem desirable. Although 200 to 300 meter columns have been fabricated and are being used in some research laboratories [179], the question remains as to whether a versatile multimember column system might be preferable to a single column for obtaining the very high chromatographic resolutions.

With the very long columns, the chromatographer should be aware of the crest concentration decay as a function of time, and this topic has been addressed in Appendix A of this report. Also, for very high efficiency OTCs (n greater than 1×10^6) one must examine the fidelity of the analytical signal generation and recording system. In short, the detection, amplification, filtration, and readout components must provide a faithful response in a system which generates the chromatographic data over an extended period of time, e.g., hundreds of minutes.

With respect to microbore OTCs, this appears to be a valuable additional tool for the future analysis of hydrocarbon fuels [180,181]. With the increased interest in fabricating microbore capillaries, considerable design attention must be given to intra- and extra-column aspects which could produce distorted elution zone profiles. The handling of output data and the presentation thereof will also require considerable attention. Some of the distortion aspects discussed in this report will be magnified when using microbore OTCs. With these columns the exit location and the temperature control throughout the chromatographic flowpath will require careful consideration. It may be that in the future special chromatographic ovens, chambers, electronic controls, pneumatic arrangements, etc. will be needed for the optimized performance of microbore OTCs. Flexible fused silica tubing for the fabrication of microbore capillaries is commercially available, and coating techniques for these columns would be somewhat similar to those used for conventional OTCs. Here again, it would be desirable for a research laboratory to have its own facility for preparing columns as this dramatically increases capabilities with respect to special experimental activities. This would especially be the case if the laboratory's work involved complex chromatographic systems which use a detailed assortment of interdependent isothermal, programmed temperature, and programmed pressure gas chromatographic modes.

Many years ago, it was claimed [182] that if a given chromatographic separation could not be obtained with an isothermal gas chromatographic column, it would likewise not be obtainable using the various forms of programmed temperature gas chromatography. This statement is probably still valid today for any particular pair of solutes. However, for very complex mixtures one may indeed want the ability to select a wide variety of different temperature programming and pressure programming modes to obtain disengagement of critical solutes. To do this work, one may also want to have the capability of fabricating almost any type of OTC that the task would require.

Conducting rapid gas chromatographic separations places special demands on the chromatographic equipment and the separation column. Microbore capillary columns are capable of performing very rapid separations [183,184], and in the near future they will probably see considerable use as integral components in multidimensional gas chromatographic systems.

Both the conventional open-tubular columns and the new microbore columns need special sample injection techniques, but most emphatically there would be a tremendous need for fast electrometers and signal recording equipment [185]. Recently, this general topic of obtaining fast analytical separations in gas chromatography [13],186] was considered by several authors from a practical standpoint and with respect to the various theoretical considerations.

4. COLUMN INSTALLATION REQUIREMENTS IN FUTURE HIGH-RESOLUTION GC SYSTEMS

The installation of HRGC columns needs increased attention. For example, problems have been reported with the breakage of fused silica OTCs when mounted on metal cages [187]. There have also been several reports of thermal nonuniformities associated with some HRGC column installations and apparently the undesirable consequences are most pronounced in the programmed temperature gas chromatographic mode [188]. Difficulties have also been reported with various elastic tubing ferrules. At elevated temperatures some polymeric organic tubing ferrules tend to gradually emit volatile degradation compounds, and after being trapped in the column interior they become contaminants in subsequent programmed temperature GC analyses [189].

Increased efforts are addressing the minimization of "ghost peaks" and associated types of contamination which can arise from the pneumatic section of the gas chromatographic instrument, the sample insertion region, and other system components which can introduce over a period of time condensible

substances that produce "false solutes" in the high-resolution chromatogram [190]. Careful consideration must be given to the selection of the diaphragm material used in pressure regulators and in flow controllers. The conditioning and cleaning of the sample insertion device is also important to obtaining contaminant-free HRGC data.

It is possible for some contaminants and ghost peaks to have their origin in the stationary phase of the open tubular column. The stationary phase can be stressed and damaged by thermal oxidation which can occur via improper filtration or purification of the carrier gas. Excessive column oven temperature can likewise degrade the stationary phase of an OTC. If numerous inappropriate samples are admitted to a column, reactions will inevitably occur and damage the stationary phase. These types of stationary phase degradation can be observed as cyclic baselines, increased column bleed levels, or spurious solutes occurring in chromatograms, particularly in the programmed temperature GC mode. Stationary phase damage can be avoided through proper installation of the column, careful conditioning of the OTC, and attention to proper chromatographic practice [191].

In the past, gas chromatographic column ovens were designed to fulfill a number of different requirements, and in doing so, designers made numerous compromises with respect to precise temperature control and the uniform distribution of turbulent air [192]. To obtain the maximum performance with fused silica OTCs and microbore capillaries, it may be necessary to reexamine the design of versatile HRGC column ovens; some recent attempts have been made at improving the thermal distribution properties in gas chromatographic ovens [193].

Uniform thermal control throughout a HRGC oven may be complicated by recent advances, wherein cold traps were used at the column inlet region [194-196]. These cryogenic trapping procedures have been most effective in condensing and localizing an injected sample. However, the control of spent coolant may

present a problem in monitoring a homogeneous thermal environment throughout the GC oven interior.

Even though liquid nitrogen (-196°C) and low-temperature carbon dioxide are used routinely as coolants, the temperature of the trapped region of the GC column can be raised to high temperatures (up to 300°C) very quickly by special heating devices and electrical heating circuits [197,198].

5. QUALITATIVE ANALYSIS AND SPECIAL INSTRUMENTATION FOR EFFLUENT DETECTION

The most popular current analytical technique for the qualitative analysis of organic compound mixtures is gas chromatography-mass spectrometry (GC-MS). In the last ten years this coupled analytical technique has been developed to a high level, and it is being used extensively in identifying individual organic compounds contained in complex matrices [199].

Several procedures have been developed for dynamically coupling a gas chromatograph and a mass spectrometer [200-202]. Considerable study has been given to the effect upon chromatographic performance when the column outlet is at very low pressure [203-205]. The performance of wide-bore OTCs of short length can be affected by installations in a GC-MS mode where the outlet is under vacuum conditions. However, by proper matching of the dimensions of the OTC to the application, such installations can be highly satisfactory.

The theoretical limitations of GC-MS have been discussed with respect to qualitative analysis, and indeed GC-MS is an especially powerful tool for identifying organic substances in complex mixtures [206]. Recently a multidimensional gas chromatographic system that can be coupled to a mass spectrometer was referred to as the most powerful combination of analytical instrumentation ever devised for separation and identification of individual components of complex mixtures. Some of the detection modes in GC-MS technology can be extremely

sensitive. For example, single ion monitoring of select fragments can permit the detection of picogram quantities of some solutes.

Other hyphenated techniques [136] which involve gas chromatography are receiving considerable attention with respect to analyzing complex organic mixtures. Stopped-flow GC-IR analysis has been introduced [207] and high interest is being given to the full development of GC-FTIR instrumentation [208-211].

At the present, an OTC-HFID can sense a hydrocarbon solute at approximately the 0.02 nanogram level, while a selective ECD may be able to sense a certain halogenated solute down to the 0.0005 nanogram region. Also, we are currently limited to approximately a 50 to 500 ng input of single solute, and in view of this relatively low sample capacity of OTCs, the only practical way of increasing the working range of present HRGC systems is to increase the sensitivity of the detection device. Accordingly, there is a continuing need for well-behaved detectors of greater sensitivity. However, even very high detector sensitivity will not compensate for solute transport shortcomings or residual adsorptivity in gas flowpaths.

Several new detectors have been introduced [212-214]. A new thermionic ionization detector and a catalytic flame ionization detector were recently demonstrated [212]. Two dedicated mass spectrometric GC detectors are now available and these detectors are essentially specially designed mass spectrometers (MS). Both of these MS detection instruments can monitor emerging solute zones that are not chromatographically separated from other solutes. They can be adjusted to respond to selected fragment ions and the analyst can preselect the detection instrument for any certain mass fragment that is to be monitored. In this manner, analytic data can be obtained for certain solutes without obtaining complete chromatographic separation. Apparently, these special MS detectors have sensitivities comparable to the HFID [213,214].

When considering a new detector for HRGC, the response time and the effective interior volume of the device are of crucial importance. Some of the more recent detectors require a reaction to take place prior to sensing the effluent. Other devices, such as the bead sensing detectors, require the occurrence of surface reactions. As some of these detection devices have inlet and exit passageways relative to the active region of the detector, they may not be adequate for advanced HRGC or rapid separation gas chromatography (RSGC), as the dead volumes and long response times [215] could adversely affect the recorded GC output resolution. The newly introduced MS detection devices have yet to be evaluated with respect to effective internal volume and response time.

6. MULTIDIMENSIONAL GAS CHROMATOGRAPHY

Much that has been discussed thus far with respect to gas chromatographic instrumentation trends has dealt with relatively fundamental approaches to obtaining increased analytical performance. The systems to be discussed hereafter are of much higher complexity, yet they have tremendous potential for separating and analyzing complex mixtures of organic compounds, e.g., hydrocarbon fuels. Essentially these systems have resulted from a systems approach to chemical analysis instrumentation, and in the future, considerable attention will be given to the design and use of analytical systems for solving detailed chemical analysis problems.

The new term "hyphenated methods", which is applied to the chemical instrumentation systems approach, involves more than just chromatography. Practically every type of chemical analysis instrument has been coupled with other instrumentation to obtain new data or to enhance simultaneous analytical information. With respect to chromatography, it is becoming increasingly clear that the chromatographs of the future will indeed be multicomponent chromatographic systems. Already

we are seeing these systems appear in different research laboratories. However, only a few basic units are presently commercially available.

For complex hydrocarbon fuels probably the most powerful technique for chromatographically separating and analyzing the various constituents is to be found in a system for multidimensional gas chromatography (MDGC). Most of the presently contemplated MDGC systems would fall into one of two classes. The first class involves both series and parallel column arrangements in which a sample is injected and transported through the column system using only unidirectional gas flow. Although this class of MDGC systems would contain a wide variety of column members, stationary phases, assorted temperature-versus-time profiles, and different gas velocities, there is no trapping of solutes or reversing the direction of gas flow. This class of MDGC systems has been with us since the early days of gas chromatography.

The second class of MDGC systems also involves multimember column arrangements; however, with this class there is extensive flow switching and even bidirectional gas flow through system members. Fraction collection followed by subsequent chromatographic processing is used extensively in this class as are multiple column ovens and special thermally controlled zones throughout the gas chromatographic flowpath [216]. This second class of MDGC systems is of most interest, and hereafter that class will be the focus of our discussion.

Basically, MDGC systems involve injecting a complex sample into one gas chromatographic column and then selectively taking fractions of that partially separated sample and passing the collected fraction through a different chromatographic column. The second chromatographic column would have different retentive properties; thus solute zones that would not be separated by the first chromatographic column would be more highly resolved by the second column. This is a very powerful technique, since there can be far more than two columns in an MDGC system.

There has been some confusion with respect to the term multidimensional chromatography. For example, two-dimensional chromatography has been applied in both paper and thin-layer chromatography for several years [218,219] and there has been some objection to using the term multidimensional merely by employing an additional elution column with a different chromatographic stationary phase.

Multidimensional systems are being contemplated for both gas chromatography and liquid chromatography. Part of the rationale behind the interest in these systems stems from the opinion that the upper limit of performance of today's conventional columns is being approached [217]. Therefore, to maximize the capabilities of existing column technology, this can be accomplished by incorporating the modern separation columns into multimember chromatographic systems.

The information content that can be obtained from an MDGC system has been studied [220] and indeed the possibilities for separating solutes are enormous. Other proposed methods for obtaining very high efficiencies or the separation of difficult solute pairs have been to use recycle chromatography [221] or, a new conceptualized procedure known as boxcar chromatography [222]. Theoretically, these two processes can produce very high separation efficiencies ($n = 10^5$ to 10^7). However, these chromatographic processes are in the planning and early research stage, and both have some difficulties to overcome before they can be put into routine practice for separating complex volatile organic mixtures. The progress made using MDGC is considerable, and the future capabilities with these instrumentation systems are most intriguing [223]. It should be recognized that an MDGC system can also be coupled to a mass spectrometer or the new tandem mass spectrometric instrumentation systems. Conceptually MDGC can be coupled in-line with FTIR instrumentation systems and many of the other hyphenated methods of instrumental chemical analysis.

The theoretical potentials for multidimensional chromatography have been studied [224] and the technology associated with MDGC has been reviewed [225,226]. The extra-column effects in MDGC have been assessed [227], and the effects of pressure and temperature upon solute behavior in coupled column systems have been investigated [228,229]. Several studies have been presented which used coupled two-column MDGC systems [230-232]. Also, a theoretical investigation was presented [233] which examined the effects of polarity change in a capillary MDGC system. A paper recently presented discussed some of the requirements to convert a conventional gas chromatographic system to a MDGC system [234]. Work has also been conducted with MDGC systems which incorporate the use of intermediate trapping [235] and a two-dimensional capillary system which did not use intermediate trapping [236]. Some very interesting recent work [237,238] has involved MDGC systems which emphasize the use of two separate ovens with different temperature versus time histories for obtaining chromatographic separations. Practically every MDGC system of the second class will use the technique known as "heart cutting" for selectively capturing and then reinserting a certain fraction of a complex sample. Several procedures used for heart cutting have been the subject of considerable research [239-242]. Recently, the quantitative aspects of MDGC were investigated [243], and the ability to convert existing chromatographic equipment to a high-resolution MDGC system [244] is most encouraging.

One "hyphenated method" that falls under the definition of multidimensional chromatography is a dynamically coupled liquid chromatograph and gas chromatograph [245-248]. Such a coupled system has advantageous analytical features for complex organics such as jet fuel, petroleum, shale oil, etc. Another mode of operation that also falls under the classification of MDGC is the use of a common injector for two or more OTCs that would be arranged in parallel, and each of these columns could then go to a different detector, in most cases detectors having

different selectivities. This is an easy technique for simultaneously obtaining, with one sample injection, an assortment of chromatographic retentive properties and different detection selectivities. A similar procedure is to use a single column going to multiple dissimilar detectors, and there has been some work in this area [249].

MDGC of the second class requires gas stream switching, and Dean's valve-free switching method has been the most popular procedure for changing the direction of gas flow. There is renewed interest in using mechanical rotary valves in MDGC and development activities have aimed at obtaining an extremely low-volume, high-temperature valve that can be used in recycle applications [250-252]. Gas stream switching has also been applied to backflush procedures [253], and there is interest in using fluidic switching in MDGC systems [254]. Better control over flow and pressure in gas flowpaths is also being achieved [255]. It has been realized that for MDGC systems to function properly, considerable attention must be given to the various coupling devices, tube fittings, junctions, tubing ferrule compositions, and any possible region of the gas flowpath which might be adsorptive or poorly swept with carrier gas [256].

One intent of a MDGC system is to conduct trace analyses. With the capability of such systems to concentrate selective fractions, this is a valid instrumental approach to conducting organic trace analyses. However, special attention must be given to quantitative sample transport [257]. To conduct trace analyses, the MDGC system would have to have excellent thermal and pneumatic control and the output data be reproducible and as free from signal noise as possible. Accordingly, within the MDGC system special attention would have to be given to the purification of the carrier gases and each of the different gas supplies that feed into in-line traps, switching devices, and the many different detectors.

Already MDGC has been used in many practical analytical applications [258], and it is encouraging to see that several of the chromatographic instrument manufacturers are now interested in supplying hardware for conducting MDGC analyses. There is a large arsenal of gas chromatographic detection devices, and as new selective and more sensitive GC detectors are introduced, this will expand the capabilities of MDGC even more. For example, trace level determinations of pesticide residues were recently conducted with a MDGC system that used a flame photometric detector [259]. Various UVD devices should also find considerable application in a MDGC system designed for fuel analysis, as it responds selectively to aromatic compounds [260] and can provide other diagnostic information. With respect to shale oil analysis, a simple form of a MDGC system was used for analyzing some of the n-heterocyclics found in shale oil [261]. Similar systems have also been used for determining alcohols in gasoline blends [262] and the analysis of volatile substances contained in a high-boiling solvent [263].

From a practical standpoint, a MDGC system should be tailored for one general type of sample. Such instrumentation systems are ideally suited for hydrocarbon fuels, as differences between fuel samples are not great. In fact, it is easy to visualize one particular MDGC procedure for analyzing JP-4 jet fuels (typically containing C_4 to C_{17} hydrocarbons) and then a slightly different MDGC system configuration for crude oil, shale oil, and other complex organic mixtures (encompassing C_4 through C_{34} hydrocarbons).

7. FUTURE PROCESSING AND TREATMENT OF HIGH-RESOLUTION GAS CHROMATOGRAPHIC DATA

One primary objective of chromatography is to obtain adequate isolation of mixture constituents so that an instrumental chemical assessment can be made of the individual solutes. Present methods for increasing solute resolution in gas chromatography involve either increasing the efficiency of the separation

column or improving selectivity [264,265] through the use of different stationary phases. Once these two routes have been thoroughly invoked and there is still insufficient chromatographic disengagement, other procedures must be applied to assess the analytical information in the chromatographic record.

Even with extremely high efficiency separation columns, there will be many instances where merged solute zones will be exiting from the chromatographic flowpath. In these cases it is important that the HRGC system be capable of faithfully describing the intracolumn chromatographic elution. Once such a precise analog signal has been generated, it is then possible to perform resolution enhancement techniques, solute zone deconvolution procedures, and for well-behaved instrumental systems it is theoretically possible to determine the number and relative concentrations of individual solutes that would be encompassed within a multicomponent elution profile. If these multicomponent elution profiles are highly distorted by nonchromatographic instrumental factors, it would be practically impossible to retrieve the valuable analytical information contained in the chromatographic output signal. With the use of special selective detection devices, mass spectrometric techniques, and other multiple peak recognition procedures [266,267] the detection of fused solutes can in principle be accomplished. However, some of these special detection devices introduce nonlinearities and can contribute to elution zone profile distortion to the extent that they may not be suitable for the rapidly eluting solutes encountered in HRGC. Even with the considerable advances underway in the field of HRGC, a major area of future activity will be the assessment and interpretation of chromatographic data where individual solute zones are only partially resolved one from the other. Consequently, the sample handling, solute transport, and output signal processing procedures are of extreme importance, and special consideration with respect to crucial chromatographic components will still be required in the HRGC systems of the future.

There has been some success using derivative techniques whereby the first, second, third, and higher derivatives of the time-based output signal have been applied for obtaining diagnostic and quantitative information. In certain instances these techniques will permit the analyst to determine if there is more than one species in an elution profile. However, in many cases these procedures will not permit an accurate measurement of the concentration of the individual solutes, nor will they determine if there are more than two solutes within a composite profile. Also, when using unfiltered derivative circuits, the signal-to-noise ratio diminishes as the order of differentiation increases. Even so, for special cases where the chromatographic resolution cannot be readily improved, analytical techniques can be undertaken using a series of higher order derivative procedures. These can be applied especially in multiple peak recognition studies [63,268-271].

In Section VIII of this report, the chromatogram of a very complex sample was presented as Figure 36. To place the entire chromatographic output signal tracing on one sheet of letter-size paper it was necessary to subdivide the chromatogram into nine different parts. By observing very closely the output signal as the chromatogram was being generated, this complex sample was found to contain more than 1,100 different chemical compounds. Figure 36 illustrates very clearly one of the more important topics relative to the future handling of HRGC data. Clearly there is a vast amount of analytical and sample specific information contained in these voltage-versus-time plots, i.e., chromatograms. Until now, practically all HRGC chromatograms have been presented in conventional Cartesian coordinates. We are now faced with the challenge of obtaining effective but convenient ways of presenting highly complex raw analytical data. Specifically, we are faced with the task of placing the maximum amount of HRGC data onto an 8 1/2" by 11" sheet of paper, thus the maximum utilization of a planar surface.

Today there are numerous data-handling systems that can process in numerical tabular form the chromatographic output data [272]. With currently available data-handling equipment we are able to store chromatographic data either within the computer or externally on magnetic tape. This information can readily be placed in archival storage, and at any future time the data can be reconstructed in a variety of different formats, most of which can be transferred onto hard copy. In many cases with the existing chromatographic computer systems, the data acquisition rate and the size of the dot matrices of the cathode ray tube limit the optical quality of the data that can eventually be displayed and transcribed to hard copy.

Some very interesting work has been conducted whereby chromatograms were displayed in circular coordinates [273] to visually distinguish subtle differences between chromatographed samples. There are several variations of the circular presentation of data that can be used for presenting HRGC data. For example, data can be displayed using a nonlinear logarithmic ordinate, as such data presentations are of value when there is interest in trace level components. For increased use of plotting area, the ordinate can also be directed inwards as opposed to projecting outwards from the center of the circular plot. Another format in which computer reconstructed HRGC data can be displayed is to have one large circular profile (possibly with logarthmic display) for the entire chromatogram and then to present each of the Kovats indices centenary representations as smaller circular coordinate plots. For example, all of the solutes eluting between n-heptane and n-octane would include all of the species having Kovats indices in the 700's. In this manner, on one sheet of paper the analyst could display in log-circular profile the major high-resolution chromatogram and with a whole series of smaller circular profiles present each of the Kovats centenary plottings of data (see Figure 39).
Such information should be quite valuable with respect to visual pattern recognition. These data can be presented in any of

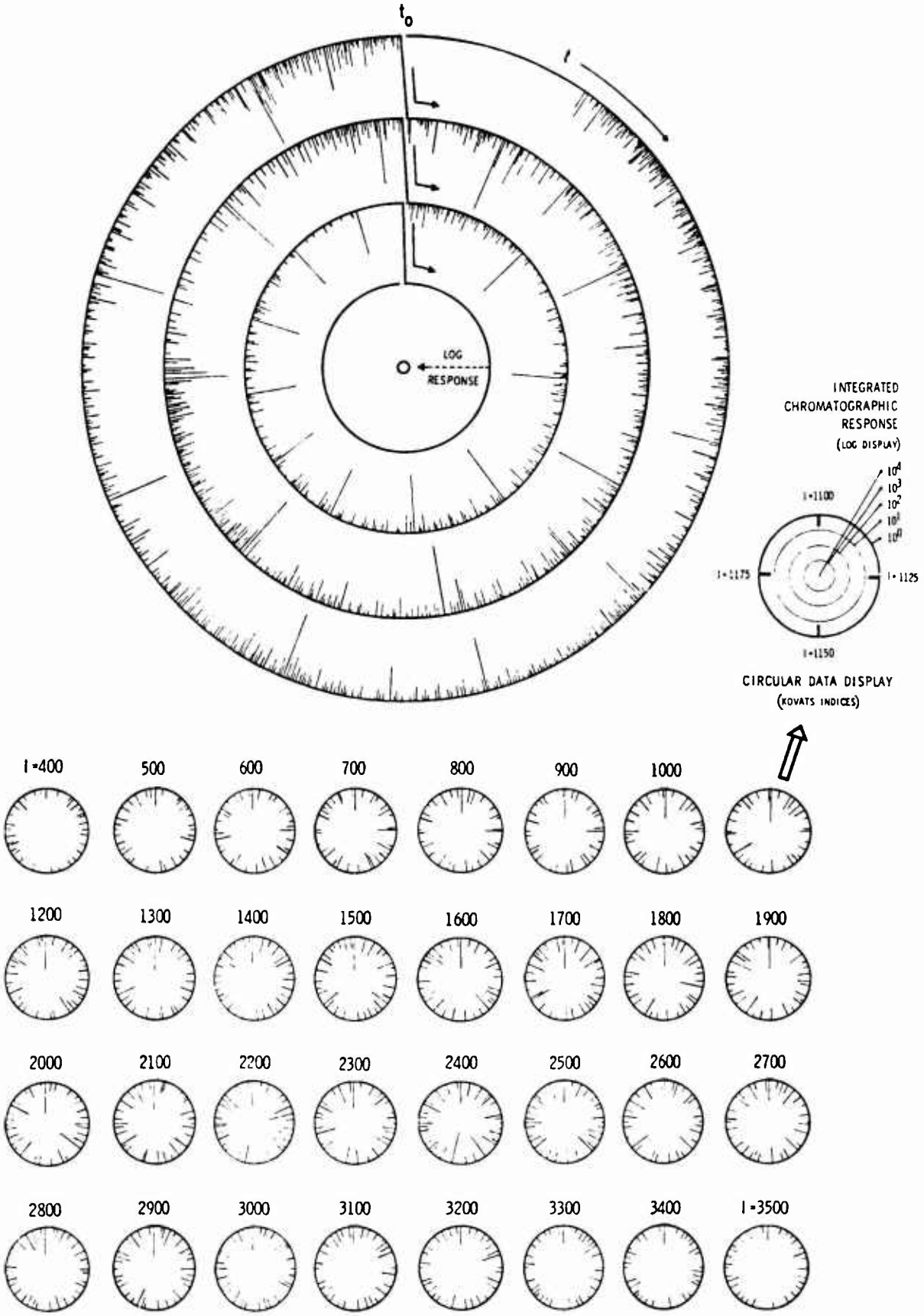


Figure 39. One possible display format for complex hydrocarbon mixtures.

several modes, e.g., linear circular display, log-circular plotting, and log-difference circular displays. Bear in mind that this is but one general method of presenting chromatographic data. There are, of course, many other methods of graphically displaying complex analytical data and these should be pursued with the objective of maximizing information content relative to display area.

In the future, we will undoubtedly see improved data handling treatments for these very complex HRGC chromatograms. The treatment of fused solute profiles will probably be handled by data systems which are specially programmed for deconvoluting multiple solute zones while at the same time performing signal enhancement procedures. Indeed, these data handling treatments are probably beyond realistic description at the present time.

The information content in a HRGC chromatogram is vast. Information theory [274] and the various chemometric procedures for processing data [275-276] hold great promise for deciphering this information and maximizing the analytical return from these highly complex voltage-versus-time functions. Statistical studies [277] of the resolution needed for separating components in HRGC indicate that although very high-efficiency columns are needed, procedures for changing chromatographic selectivity and the elution behavior of solutes are important. The processing of HRGC data using computer-enhanced high-resolution procedures in conjunction with pattern recognition techniques can provide an enormous amount of information concerning multicomponent organic mixtures [278].

The application of chemometrics to the analysis of hydrocarbon fuels would seem to have considerable application, particularly with respect to isolating and measuring those crucial compounds and chemical variables which influence the various quality aspects of hydrocarbon fuels. Chemometrics, in conjunction with a special dedicated HRGC system, would seem to be an ideal investigative mechanism for studying and monitoring important minor fuel constituents, changes in fuel composition,

subtle long-term reactions, and other chemical aspects that can have a pronounced effect upon the quality of hydrocarbon fuels.

With respect to the future analysis of complex organic mixtures, e.g., hydrocarbon fuels, one can visualize a specially designed and dedicated multidimensional HRGC system that uses a variety of high performance columns along with numerous different detection devices and has access to advanced mass spectrometric instrumentation. This HRGC facility will have computer routines for deconvoluting fused solutes and performing chemometric procedures on the resultant data.

SECTION X

DISCUSSION AND RECOMMENDATIONS

Several guidelines and recommendations can be set forth to advance the analytical capability for analyzing turbine engine fuels and their various precursors. While many of these recommendations are straightforward and can be applied in any analytical laboratory that is involved with complex organic mixtures, some are quite specific with respect to the analysis of jet fuel, crude oil, shale oil, liquified coal, and other geochemical feedstocks. These guidelines and recommendations are as follows:

(1) Any practice whereby the complexity of the sample can be simplified is of merit in chromatography. Preparative separations and classifications can simplify the subsequent chromatographic separation of a highly complex organic mixture; although, this practice tends to affect the total accuracy of the analysis, as invariably there seems to be some loss of constituents during preseparation processing.

(2) To obtain the maximum resolution and also generate precise qualitative gas chromatographic data, the system must not be overloaded. Therefore, it is necessary that only a small amount of total sample be admitted to the open tubular separation column.

(3) It is necessary to have extremely clean carrier gases to perform trace level analyses while avoiding misleading (false) GC information, e.g., ghost peaks, signal noise, baseline disturbances, and improper digitization. The upstream components must be specially selected so that they do not contribute trace level organics to the resultant analysis. The cleanliness of the entire GC system should be routinely tested through the use of analytical blanks.

(4) For a laboratory that is engaged in state-of-the-technology HRGC, some consideration should be given to establishing its own capability for preparing special open tubular columns, e.g., microbore OTCs, columns with different film thicknesses, and special stationary-phase columns.

(5) Within any HRGC system, considerable attention should be given to the thermal control of various components, such as the injector, the detector, and their respective connectors. Thermal gradients must be avoided in the vicinity of the separation column. Also, there should not be any cyclic heating and cooling associated with the separation column.

(6) Hydrogen carrier gas is definitely recommended for narrow-bore OTCs. This carrier gas is advantageous both in programmed temperature GC operation and in performing rapid separation gas chromatography. However, definite precautions must be taken to insure that hydrogen gas cannot inadvertently or accidently be admitted to the hot GC oven.

(7) Each important component in the chromatographic flowpath should be studied and optimized utilizing a systems approach so that concentration zone profile symmetry is maintained throughout. Attention should be given to (a) the detector configuration and its associated adapters, (b) a protective screen or perforated lid on the detector exit, (c) examination of the various exponential decay time constants that may be encountered with both the gas flowpath and the instrument electronics, and (d) optimization of the overall system response behavior.

(8) The many benefits of multidimensional gas chromatography (MDGC) are definitely recommended for a laboratory that is involved with analyzing complex organic mixtures. Although MDGC is more involved with respect to hardware and electronics, its benefits far outweigh the increase in complexity presented by the equipment. For a laboratory that works with relatively similar samples MDGC has much to offer. Time normalization procedures can be utilized with such a system, as can pressure programming techniques. Specially dedicated MDGC instrumentation systems can be assembled for conducting ultra high-resolution gas chromatographic separations.

(9) It is recommended that further work be conducted in establishing different operational mechanisms for disengaging solute zones. This would involve the investigation of different temperature programming rates in conjunction with different carrier gas velocities and their effects upon solute resolution.

(10) Effluent splitters can be used advantageously in some installations involving dissimilar detectors. However, effluent splitters can detract from the maximum available chromatographic resolution.

(11) A HRGC system that is capable of producing symmetrical elution zone profiles and low noise output signals which can be sampled at a rapid rate, e.g., greater than 10 Hz, is highly amenable to the development of resolution enhancement techniques and solute zone deconvolution procedures. With a suitably sized computer, such digitized data are ideally suited for sophisticated chemometric studies, and thus, a high level of the total information content can be extracted.

(12) It is recommended that consideration be given to enhanced methods for displaying the abundant information that is contained in the HRGC readout. Improved procedures for formatting chromatograms are needed.

In Volume II of this report, there are additional recommendations and discussions with respect to the sample insertion process for HRGC.

REFERENCES

1. Military Specification MIL-T-5624L, Aviation Turbine Fuel, Grades JP-4 and JP-5, Issued 18 May 1979.

2. C. C. Gleason and J. A. Martone, Pollutant Emission Characteristics of Future Aviation Jet Fuels, J. Air Poll. Control Assoc., 29: 1243, 1979.

3. J. D. Bittner and J. B. Howard, Role of Aromatics in Soot Formation, In: Alternative Hydrocarbon Fuels--Combustion and Chemical Kinetics, C. T. Bowman and J. Birkeland, eds., AIAA Progress in Astronautics and Aeronautics, Vol. 62, 1978.

4. W. S. Blazowski and L. Maggitti, Future Fuels in Gas Turbine Engines, In: Alternative Hydrocarbon Fuels--Combustion and Chemical Kinetics, C. T. Bowman and J. Birkeland, eds., AIAA Progress in Astronautics and Aeronautics, Vol. 62, 1978.

5. L. C. Angello, A. V. Churchill, C. L. Delaney, and H. R. Lander, Shale Oil - The Answer to the Jet Fuel Availability Question, SAE Paper No. 781027, Presented at the SAE Aerospace Meeting, San Diego, CA, November, 1978.

6. E. N. Coppola, D. D. Potter, R. N. Butler, and E. M. Conley, Military Jet Fuel from Shale Oil, Paper presented at IGT Symposium held in Atlanta, GA, December, 1979.

7. Chemical and Engineering News, September 15, 1980, p. 41

8. H. R. Lander, Jr., Jet Fuel from Shale Oil - 1981 Technology Review, Report AFWAL-TR-81-2135, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, OH, November, 1981.

9. F. D. DiSanzo, P. C. Uden, and S. Siggia, Isolation and Identification of Light Oil Alkanes in Shale Oil by Vapor Phase Reaction/Gas Chromatography, Anal Chem., 51:1529, 1979.

10. F. P. DiSanzo, P. C. Uden, and S. Siggia, Shale Oil Hydrocarbon Separation by Preparative Liquid Chromatography and Glass Capillary Gas Chromatography, Anal Chem., 52:906, 1980.

11. H. S. Hertz, J. M. Brown, S. N. Chesler, F. R. Guenther, L. R. Hilpert, W. E. May, R. M. Parris, and S. A. Wise, Determination of Individual Organic Compounds in Shale Oil, Anal. Chem., 52:1650, 1980.

12. R. T. Crowley, S. Siggia, and P. C. Uden, Class Separation and Characterization of Shale Oil by Liquid Chromatography and Capillary Column Gas Chromatography, Anal. Chem., 52:1224, 1980.

13. G. R. Cooper and C. D. McGillem, Methods of Signal and System Analysis, Holt, Rinehart, and Winston, New York, NY, 1967.

14. G. Schomburg, Practical Limitations of Capillary Gas Chromatography, HRC & CC, 2:461, 1979.

15. H. Purnell, Gas Chromatography, Wiley and Sons, New York, NY, 1962.

16. S. Dal Nogare, and R. S., Juvet, Jr., Gas-Liquid Chromatography, Interscience, New York, NY, 1962.

17. J. Novak, Quantitative Analysis by Gas Chromatography, Marcel Dekker, New York, NY, 1975.

18. W. A. Rubey, Design of a System for Simultaneous Thermogravimetric-Gas Chromatographic Analysis of Stabilized Polyacrylonitrile Fiber, University of Dayton Research Institute Technical Report, UDRI-TR-71-28, September, 1971.

19. P. W. Centers and W. A. Rubey, An Experimental Approach to High-Resolution Gas-Liquid Chromatography for High Molecular Weight Compounds, Report AFAPL-TR-68-137, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, OH, November, 1968.

20. G. H. L. Ehlers, W. A. Rubey, and D. S. Duvall, Isothermal Decomposition Studies of Aromatic and Heterocyclic Polymers in Air, Report for Air Force Materials Laboratory, AFML-TR-76-93, June, 1976.

21. W. A. Rubey, Design Considerations for a Thermal Decomposition Analytical System (TDAS), Report for U.S. Environmental Protection Agency, EPA-600/2-80-098, August, 1980.

22. Preferred Stationary Liquids for Gas Chromatography, J. Chromatog. Sci., 13:115, 1975.

23. G. Schomburg, Sampling Systems in Capillary Chromatography, Paper presented at Fourth International Capillary Chromatography Symposium, Hindelang, Germany, May, 1981.

24. Symposium on Injection Techniques in Capillary Gas Chromatography, Held in Frankfurt, Germany, October, 1982.

25. M. J. E. Golay, Theory and Practice of Gas Liquid Partition Chromatography with Coated Capillaries, In: Gas Chromatography, V. C. Coates, ed., Academic Press, New York, NY, 1958.

26. M. J. E. Golay, Theory of Chromatography in Open and Coated Tubular Columns with Round and Rectangular Cross Sections, In: Gas Chromatography 1958, D. H. Desty, ed., Butterworths, London, 1958.

27. J. Schieke, N. Comins, and V. Pretorius, Whiskers: A New Support for Glass Open Tubular Columns in Gas Chromatography, Chromatographia, 8:354, 1975.

28. M. J. E. Golay, Gas Chromatography with Open Tubular Columns - Past and Present, Paper presented at 1981 American Chemical Society Meeting held in Atlanta, GA, March, 1981.

29. M. J. E. Golay, The Height Equivalent to a Theoretical Plate of Retentionless Rectangular Tubes, J. Chromatog., 216:1, 1981.

30. R. D. Dandeneau and E. H. Zerenner, An Investigation of Glasses for Capillary Chromatography, HRC & CC, 2:351, 1979.

31. P. F. Bente, III, E. H. Zerenner, and R. D. Dandeneau, (assigned to Hewlett-Packard Co.), Silica Chromatographic Column, U.S. Patent 4,293,415 (1981).

32. M. Novotny and K. Bartle, Surface Chemistry of Glass Open Tubular Columns Used in Gas-Liquid Chromatography, Chromatographia, 7:122, 1974.

33. W. E. Dirkes, Jr., W. A. Rubey, and C. G. Pantano, The Formation of a Silica-Rich Surface Using Sulfur Dioxide in Drawn Glass Capillaries, HRC & CC, 3:303, 1980.

34. C. Madani, E. Chambaz, M. Rigaud, J. Durand, and P. Chebroux, New Methods for the Preparation of Highly Stable Polysiloxane - Coated Glass Open-Tubular Capillary Columns and Application to the Analysis of Hormonal Steroids, J. Chromatog., 126:161, 1976.

35. L. Blomberg, J. Buijten, K. Markides, and T. Wannman, Evolution of Bonded Methylsilicone Rubber as a Stationary Phase for Glass Capillary Columns, J. Chromatog., 208:231, 1981.

36. L. Blomberg, J. Buijten, J. Gawdzik, and T. Wannman, Preparation of Thermostable Phenyl Silicone Coated Glass Capillary Columns for Separation of Polyaromatic Hydrocarbons, Chromatographia, 11:521, 1978.

37. F. I. Onuska and M. E. Comba, Preparation and Application of Surface-Modified High-Resolution Wall-Coated Open Tubular Columns, J. Chromatog., 126:133, 1976.

38. R. F. Arrendale, R. F. Severson, and O. T. Chortyk, Preparation of Wall-Coated Open Tubular (Pyrex) Capillary Columns with Polar Stationary Phases Using Superox-4 as a Surface Pretesting and Deactivating Agent, J. Chromatog., 208:209, 1981.

39. V. Pretorius and J. W. DuToit, Gas Chromatography in Glass and Fused Silica Capillary Columns: Deactivation of the Inner Surface Using Silicon Films, HRC & CC, 4:344, 1981.

40. J. H. Purnell, Correlation of Separating Power and Efficiency of Gas Chromatographic Columns, J. Chem. Soc., (London) 1268, 1960.

41. L. Sojak, J. Krupcik, and J. Janak, Gas Chromatography of All C_{15} to C_{18} Linear Alkanes on Capillary Columns with Very High Resolution Power, J. Chromatog., 195:43, 1980.

42. A. Robinson, D. Partridge, M. Turner, R. Teranishi, and L. Pauling, An Apparatus for the Quantitative Analysis of Volatile Compounds in Urine, J. Chromatog., 85:19, 1973.

43. B. W. Wright and M. L. Lee, Rapid Analysis Using Short Capillary Columns in Gas Chromatography, HRC & CC, 3:352, 1980.

44. T. A. Rooney, L. H. Altmayer, R. R. Freeman, and E. H. Zerenner, Rapid GC Separations Using Short Glass Capillary Columns, Paper presented at 1978 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

45. A. B. Littlewood, Gas Chromatography: Principles, Techniques, and Applications, Academic Press, New York, NY, 1970.

46. J. A. Perry, Introduction to Analytical Gas Chromatography: History, Principles, and Practice, Marcel Dekker, New York, NY, 1981.

47. B. Karger, A Critical Examination of Resolution Equations for Gas-Liquid Chromatography, J. Gas Chromatog., 5:161, 1967.

48. W. Jennings, Gas Chromatography with Glass Capillary Columns, Academic Press, New York, NY, 1978.

49. K. Grob, G. Grob, and K. Grob, Jr., Testing Capillary Gas Chromatographic Columns, J. Chromatog., 219:13, 1981.

50. J. Krupcik, J. Garaj, G. Guiochon, and J. M. Schmitter, On the Use of the Separation Number as a Criterion for the Evaluation of Gas Chromatography Capillary Columns in Isothermal Conditions, Chromatographia, 14:501, 1981.

51. W. Jennings and K. Yabumoto, Effect of Test Temperature on Separation Number, HRC & CC, 3:177, 1980.

52. W. Bertsch, V. Pretorius, and K. Lawson, Activity Testing of Capillary Columns for GC: The "Intermediate Test" Method and the Necessary Length of the Test Column, HRC & CC, 5:568, 1982.

53. R. C. M. DeNijs and R. P. M. Dooper, Intermediate Test for (Fused Silica) Capillary Columns, HRC & CC, 3:583, 1980.

54. K. Grob and G. Grob, Separation Efficiency Versus Column Length: An Experimental Study with Capillary Columns, J. Chromatog. Sci., 7:515, 1969.

55. J. Novak, Effects of the Column Length on the HETP in Gas Chromatography, J. Chromatog., 50:385, 1970.

56. K. Yabumoto and W. J. A. Vandenheuvel, Optimization of Operating Parameters for Glass Capillary Column Gas Chromatography, J. Chromatog., 140:197, 1977.

57. R. R. Freeman, High Resolution Gas Chromatography, 1st Edition, Hewlett-Packard Co., 1979.

58. L. S. Ettre, Selection of Carrier Gas Velocity in the Analysis of a Multicomponent Sample, Chromatographia, 12:509, 1979.

59. J. G. Moncur, T. E. Sharp, and E. R. Byrd, Focused Cryogenic Trapping for Dynamic Headspace and Pyrolytic Analysis of Polymers on a Fused Silica Capillary Column, HRC & CC, 4:603, 1981.

60. G. Schomburg and G. Dielman, Identification by Means of Retention Parameters, J. Chromatog. Sci., 11:151, 1973.

61. V. A. Gerasimenko, K. V. Kirilenko, and V. M. Nabivach, Capillary Gas Chromatography of Aromatic Compounds Found in Coal Tar Fractions, J. Chromatog., 208:9, 1981.

62. J. Rijks, J. Van den Berg, and J. Diependaal, Characterization of Hydrocarbons in Complex Mixtures by Two-Dimensional Precision Gas Chromatography, J. Chromatog., 91:603, 1974.

63. W. A. Rubey, The Measurement of Concentration Zone Profile in Elution Chromatography, Technical Report UDRI-TR-70-45, University of Dayton Research Institute, Dayton, OH, December, 1970.

64. J. R. Conder, Peak Distortion in Chromatography, Part 1: Concentration-Dependent Behavior, HRC & CC, 5:341, 1982.

65. J. R. Conder, Peak Distortion in Chromatography, Part 2: Kinetically Controlled Factors, HRC & CC, 5:397, 1982.

66. M. Goedert and G. Guiochon, Investigation of the Effects of Temperature Gradients and Fluctuations on Gas Chromatographic Retention Data, Anal. Chem., 45:1180, 1973.

67. Discussion with M. L. Lee of Brigham Young University, June, 1979.

68. F. H. Pollard and C. J. Hardy, A Preliminary Study of Some Factors Influencing the Order of Elution of Halogenated Methanes, The Degree of Separation, and the Reproducibility of Retention Volumes in Gas-Liquid Partition Chromatography, In: Vapour Phase Chromatography, D. H. Desty, and C. L. A. Harbourn, eds., Butterworths, London, 1957.

69. K. Yabumoto, D. F. Ingraham, and W. G. Jennings, The Overload Phenomenon in Gas Chromatography, HRC & CC, 3:248, 1980.

70. V. Pretorius and T. W. Smuts, Sample Capacity in Open Tubular and Micro-Packed Columns for GC, HRC & CC, 2:444, 1979.

71. P. C. Haarhoff and H. J. Van der Linde, Concentration Dependence of Elution Curves in Non-Ideal Gas Chromatogrpahy, Anal. Chem., 38:573, 1966.

72. Discussion with R. R. Freeman of the Hewlett-Packard Co., June, 1982.

73. S. Dal Nogare and R. S. Juvet, Jr., Gas-Liquid Chromatography, Interscience, New York, NY, 1962, p. 322.

74. W. E. Harris and H. W. Habgood, Programmed Temperature Gas Chromatography, Wiley, New York, NY, 1966.

75. J. E. Oberholtzer and L. B. Rogers, Precise Gas-Chromatographic Measurements, Anal. Chem., 41:1234, 1969.

76. M. Goedert and G. Guiochon, Sources of Error in Measurement of Retention Times, Anal. Chem., 42:962, 1970.

77. G. Schomburg, Trends in Capillary Gas Chromatography, Paper presented at 1983 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

78. S. A. Mooney, Gas Chromatographic Peak Splitting Due to Subambient Accessory, HRC & CC,5:507, 1982.

79. W. Jennings, Troubleshooting New Capillary GC Hardware, Paper presented at 1983 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

80. D. T. David, Gas Chromatographic Detectors, Wiley, New York, 1974.

81. J. Sevcik, Detectors in Gas Chromatography, Elsevier Scientific, New York, 1976.

82. J. C. Sternberg, Detection Devices for Gas Chromatography, In: Gas Chromatography, L. Fowler, ed., Academic Press, New York, 1963.

83. L. S. Ettre, Selective Detection in Column Chromatography, J. Chrom. Sci., 16:396, 1978.

84. S. O. Farwell, D. R. Gage, and R. A. Kagel, Current Status of Prominent Selective Gas Chromatographic Detectors: A Critical Assessment, J. Chrom. Sci., 19:358, 1981.

85. J. Connor, The Electron-Capture Detector, Part I: Theoretical Model, J. Chromatog., 200:15, 1980.

86. J. Connor, The Electron-Capture Detector, Part II: Design and Performance, J. Chromatog., 210:193, 1981.

87. F. J. Yang and S. P. Cram, Characteristics and Performance of Gas Chromatographic Detectors with Glass Capillary Columns, HRC & CC, 2:487, 1979.

88. S. Kapila and C. R. Vogt, A Gas-Tight Low-Volume Photoionization Detector for Capillary Gas Chromatography, HRC & CC, 4:233, 1981.

89. A. N. Freedman, The Photoionization Detector: Theory, Performance, and Application as a Low-Level Monitor of Oil Vapor, J. Chromatog., 190:263, 1980.

90. A. Sodergren, Simultaneous Detection of Halogenated and Other Compounds by Electron-Capture and Flame-Ionization Detectors Combined in Series, J. Chromatog., 160:271, 1978.

91. P. Gagliardi, G. R. Verga, and F. Munari, A Multidetector GC System for High-Resolution Head-Space Analysis, Amer. Lab., May, 1981, p. 82.

92. J. R. Dahlgran, Simultaneous Detection of Total and Halogenated Hydrocarbons in Complex Environmental Samples, HRC & CC, 4:393, 1981.

93. W. A. McKinley, R. J. Anderson, and P. W. Thiede, Simultaneous Analysis with the Photoionization Detector and Hall Electrolytic Conductivity Detector, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

94. W. A. Rubey, Peak Height as the Quantitation Parameter in Rapid Separation Gas Chromatography, University of Dayton Research Institute Technical Report, UDRI-TR-72-117, April, 1972.

95. J. Novak, Quantitative Analysis by Gas Chromatography, Marcel Dekker, New York, 1975, p. 161.

96. J. C. Giddings, Dynamics of Chromatography, Part I: Principles and Theory, Marcel Dekker, New York, 1965.

97. G. Gaspar, P. Arpino, and G. Guiochon, Study in High-Speed Gas Chromatography, Part I: Injection of Narrow Sample Plugs, J. Chrom. Sci., 15:256, 1977.

98. J. C. Sternberg, W. S. Gallaway, and D. T. L. Jones, The Mechanism of Response of Flame Ionization Detectors, In: Gas Chromatography, W. Brenner, J. E. Callen, and M. D. Weiss, eds., Academic Press, New York, 1962.

99. J. Sevcik, Detectors in Gas Chromatography, Elsevier Scientific, New York, 1976, Chap. 5.

100. A. T. Blades, The Flame Ionization Detector, J. Chrom. Sci., 11:251, 1973.

101. I. G. McWilliam, Linearity and Response Characteristics of the Flame Ionization Detector, J. Chromatog., 6:110, 1961.

102. K. Grob, Jr., Stability of the FID Sensitivity During an Analysis in Capillary GC, HRC & CC, 3:286, 1980.

103. W. Jennings, Gas Chromatography with Glass Capillary Columns, 2nd Edition, Academic Press, 1980.

104. V. Lopez-Avila, Analysis of Sludge Extracts by High Resolution GC with Selective Detectors, HRC & CC, 3:545, 1980.

105. F. J. Yang, Column Effluent Splitter for High Resolution Gas Chromatography, J. Chrom. Sci., 19:523, 1981.

106. B. W. Later, B. W. Wright, and M. L. Lee, Construction of an Efficient Fused Silica Capillary Column Effluent Splitter for Gas Chromatography, HRC & CC, 4:406, 1981.

107. T. H. Parliment, Capillary Gas Chromatographic Analysis of N and S Compounds, Amer. Lab., May, 1982, p. 35.

108. K. D. Steele and J. A. Zabkiewicz, Inner Surface Deterioration in Glass-Lined Tubing, J. Chromatog., 174:434, 1979.

109. R. G. Ackman and J. C. Sipos, Small Components in GLC Analysis: The Benefits of Replacement of Metal Tubing Connectors with Glass-Lined Metal Tubing, J. Chrom. Sci., 14:568, 1978.

110. D. A. Miller and E. P. Grimsrud, Analysis Errors Following Hydrogen Cleaning of an Electron Capture Detector, J. Chromatog., 190:133, 1980.

111. K. Grob, Practical Capillary Gas Chromatography - A Systematic Approach, Paper presented at 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

112. H. W. Johnson, Jr., The Quantitative Interpretation of Gas Chromatographic Data, In: Advances in Chromatography, Volume 5, J. C. Giddings and R. A. Keller, eds., Marcel Dekker, New York, 1968.

113. D. H. Desty, A Goldup, and W. T. Swanton, Performance of Coated Capillary Columns, In: Gas Chromatography, N. Brenner, J. E. Callen, and M. D. Weiss, eds., Academic Press, New York, 1962.

114. R. L. Wade and S. P. Cram, Quantitative Interpretation of Semilogarithmic Gas Chromatographic Data, Anal. Chem., 41:893, 1969.

115. W. D. Ross, W. J. Hillan, K. A. Flayler, J. V. Pustinger, J. J. Brooks, and K. J. Eisentraut, Use of Circular Profiling Techniques in Gas Chromatography, J. Chromatog. Sci., 15:461, 1977.

116. E. B. Overton, C. F. Steele, and J. L. Laseter, Computer Reconstruction of High Resolution Gas Chromatograms, HRC & CC, 1:109, 1978.

117. G. Janssens, Computer Reconstructed Gas and Liquid Chromatograms, HRC & CC, 2:84, 1979.

118. G. Janssens and H. Beernaert, Computer Supported Comparison of Gas Chromatographic Analyses, HRC & CC, 3:326, 1980.

119. J. T. Lundeen and R. S. Juvet, Jr., Quantitative Resolution of Severely Overlapping Chromatographic Peaks, Anal. Chem., 53:1369, 1981.

120. M. Rosenbaum, V. Hancil, and R. Komers, Resolution of Overlapping Chromatographic Peaks with an Interfering Background, J. Chromatog., 246:1, 1982.

121. P. Tarroux and T. Rabilloud, Complete Computer System for Processing Chromatographic Data, J. Chromatog., 248:249, 1982.

122. A Strickler and W. S. Gallaway, Analog Integration Techniques in Chromatographic Analysis, J. Chromatog., 5:185, 1961.

123. W. Kipiniak, A Basic Problem - The Measurement of Height and Area, J. Chromatog. Sci., 19:332, 1981.

124. J. B. Phillips, Signal Processing Techniques in Analytical Instruments, Trends in Anal. Chem., 1(7) 163, 1982.

125. P. C. Hayes, Jr. and E. W. Pitzer, Characterizing Petroleum and Shale-Derived Jet Fuel Distillates Via Temperature-Programmed Kovats Indices, J. Chromatog., 253:179, 1982.

126. J. K. Haken, Retention Indices in Gas Chromatography, In: Advances in Chromatography, Volume 14, J. C. Giddings and R. A. Keller, eds., Marcel Dekker, New York, NY, 1977.

127. P. Majlat, Z. Erdos, and J. Takacs, Calculation and Application of the Retention Indices in Programmed-Temperature Gas Chromatography, J. Chromatog., 91:89, 1974.

128. F. J. Yang and S. P. Cram, The Theoretical and Practical Ranges of Capillary Gas Chromatography, Paper presented at 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

129. J. Franzen, Theory of GC^2 - An Unusual Approach, HRC & CC, 2:324, 1979.

130. J. C. Giddings, Future Pathways for Analytical Separations, Anal. Chem., 53:945A, 1981.

131. J. C. Giddings, Basic Approaches to Separation: Steady-State Zones and Layers, Sep. Sci., 14:871, 1979.

132. G. Guiochon, Comparison of the Theoretical Limits of Separating Speed in Liquid and Gas Chromatography, Anal. Chem., 52:2002, 1980.

133. M. J. E. Golay, The Dynamic Diffusion Constant Within Fluid Flow in an Open Straight Tube with an Elliptical Cross-Section, J. Chromatog., 196:349, 1980.

134. M. Martin, J. L. Jurado-Baizaval , and G. Guiochon, Gas Chromatography in Open Rectangular Channels with Large Aspect Ratios, Chromatographia, 16:98, 1983.

135. M. Lee, The Future of Capillary Column Gas Chromatography - An Introduction, Paper presented at 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

136. T. Hirschfeld, The Hy-phen-ated Methods, Anal. Chem., 52:297A, 1980.

137. J. W. Jorgenson and K. D. Lukas, Zone Electrophoresis in Open-Tubular Glass Capillaries, Anal. Chem., 53:1298, 1981.

138. J. B. Phillips, Multiplex Gas Chromatography, Anal. Chem., 52:468A, 1980.

139. M. Novotny, S. R. Springston, P. A. Peaden, J. C. Fjeldsted, and M. L. Lee, Capillary Supercritical Fluid Chromatography, Anal. Chem., 53:407A, 1981.

140. P. A. Peaden, J. C. Fjeldsted, M. L. Lee, S. R. Springston, and M. Novotny, Instrumental Aspects of Capillary Supercritical Fluid Chromatography, Anal. Chem., 54:1090, 1982.

141. R. D. Smith, W. D. Felix, J. C. Fjeldsted, and M. L. Lee, Capillary Column Supercritical Fluid Chromatography/Mass Spectrometry, Anal. Chem., 54:1883, 1982.

142. J. C. Fjeldsted, W. P. Jackson, P. A. Peaden, and M. L. Lee, Density Programming in Capillary Supercritical Fluid Chromatography, J. Chromatog. Sci., 21:222, 1983.

143. P. L. Peaden and M. L. Lee, Theoretical Treatment of Resolving Power in Open Tubular Column Supercritical Fluid Chromatography, J. Chromatog., 259:1, 1983.

144. B. E. Wenzel, Chromatography Needs: The Industrial Petrochemical/Fuel Lab, J. Chromatog. Sci., 20:409, 1982.

145. F. L. Bayer, An Overview of Chromatographic Instrumentation: Problems and Solutions, J. Chromatog. Sci., 20:393, 1982.

146. S. M. Sonchik, Chromatographic Needs of the Environmental Chemist, J. Chromatog. Sci., 20:402, 1982.

147. L. E. Green and E. Matt, P.O.N.A. Analysis by High Resolution Fused Silica Gas Chromatography, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

148. M. Verzele, The Choice of the Stationary Phase in Capillary GC or The More Popular GC Phase are Not Necessarily Best for $(GC)^2$, HRC & CC, 1:288, 1978.

149. K. Grob and G. Grob, Capillary Columns with Very Thick Coatings, HRC & CC, 6:133, 1983.

150. F. P. DiSanzo, P. C. Uden, and S. Siggia, Isolation and Identification of Light Oil Alkanes in Shale Oil by Vapor Phase Reaction/Gas Chromatography, Anal. Chem., 51:1529, 1979.

151. C. Wiley, M. Iwao, R. N. Castle, and M. L. Lee, Determination of Sulfur Heterocycles in Coal Liquids and Shale Oils, Anal. Chem., 53:400, 1981.

152. D. M. Parees and A. Z. Kamzelski, Characterization of Coal-Derived Liquids Using Fused Silica Capillary Column GC-MS, J. Chromatog. Sci., 20:441, 1982.

153. R. J. Phillips, Routine Analysis of Volatile Components in Foods and Beverages, Amer. Lab., 15(7) 2, 1983.

154. L. S. Ettre, J. E. Purcell, J. Widomski, B. Kolb, and P. Pospisil, Investigation on Equilibrium Headspace-Open Tubular Column Gas Chromatography, J. Chromatog. Sci., 18:116, 1980.

155. R. A. Zweidinger, J. Albert, and E. D. Pellizzari, Fractionation of Wastewater Extracts for Capillary Gas Chromatography/Mass Spectrometry Analysis, Paper presented at American Chemical Society meeting held in Las Vegas, NV, March 1982.

156. D. W. Later, M. L. Lee, K. D. Bartle, R. C. Kong, and D. L. Vassilaros, Chemical Class Separation and Characterization of Organic Compounds in Synthetic Fuels, Anal. Chem., 53:1612, 1981.

157. K. J. Bombaugh, D. H. Rodgers, and J. C. Beltz, Chromatographic Separation of Conventional and Experimental Fuels, Report AFWAL-TR-80-2098, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, OH, October, 1980.

158. W. B. Innes, W. E. Bambrick, and A. J. Andreatch, Hydrocarbon Gas Analysis Using Differential Chemical Absorption and Flame Ionization Detectors, Anal. Chem., 35:1198, 1963.

159. D. M. Jewell, Synthetic Fuels, In: Chromatography in Petroleum Analyses, K. H. Altgert and T. H. Gouw, eds., Marcel Dekker, New York, NY, 1979.

160. Anal. Chem., 52:481A, 1980.

161. J. Roeraade and C. R. Enzell, Preparative Gas Chromatography with Glass Capillary Columns, HRC & CC, 2:123, 1979.

162. A. Zlatkis, F. S. Wang, and H. Sanfield, Trace Gas Chromatographic Analysis by Use of Large Sample On-Column Injection with Bonded Phase Capillary Columns, Anal. Chem., 54:2406, 1982.

163. H. Borwitzky and G. Schomburg, Influence of Elution Temperature and Polarity of Different Stationary Liquids on the Resolution of the Diastereomers on Norpristane, Pristane, and Phytane, J. Chromatog., 240:307, 1982.

164. J. Albaiges, J. Borbon, and M. Gassiot, Gas Chromatographic-Mass Spectrometric Indentification of Geochemically Significant Isoalkane Hydrocarbons, J. Chromatog., 204:491, 1981.

165. G. Matsumoto and T. Hanya, Presence of Squalane in Urban Aquatic Environments, J. Chromatog., 194:199, 1980.

166. J. G. Bendoraitis, B. L. Brown, and L. S. Hepner, Isoprenoid Hydrocarbons in Petroleum, Anal. Chem., 34:49, 1962.

167. W. Heller, M. Schallies, and K. Schmidt, Gas-Liquid Chromatographic-Mass Spectrometric Studies on Extracts and Distillates from Posidonomia Shales, In: Advances in Chromatography 1979, A. Zlatkis, ed., University of Houston, Houston, TX, 1979.

168. H. Nakagawa, S. Tsuge, T. Itho, and M. Kimoto, Characterization of Hydrocarbon Waxes by Gas-Liquid Chromatography with a High-Resolution Glass Capillary Column, J. Chromatog., 260:391, 1983.

169. R. G. Schaefer and H. Pooch, Thermal Mobilization of Hydrocarbons from Small-Size Rock Samples: Application in Petroleum Geochemistry, Chromatographia, 16:257, 1982.

170. C. E. R. Jones and N. E. Vanderborgh, Elucidation of Geomatrices by Laser Pyrolysis-Gas Chromatography and Pyrolysis-Mass Spectrometry, In: Advances in Chromatography 1979, A. Zlatkis , ed., University of Houston, Houston, TX, 1979.

171. W. A. Rubey, L. Krishnamurthy, and W. E. Dirkes, Jr., Some Preliminary Theoretical and Experimental Studies on Undulated Open Tubular Flow Paths, Report AFWAL-TR-82-2077, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, OH, September, 1982.

172. D. Yun-Yu and L. Shu-Xin, Glass Capillary Column of Quincuncial Cavity: Its Drawn-Forming and Preliminary Performance, In: Proceedings of Fourth International Symposium on Capillary Chromatography, Hindelang, Germany, May, 1981.

173. R. Tijssen and R. T. Wittebrood, Effect of Column-Coiling on the Dispersion of Solutes in Gas Chromatography, Part II: General Theory, Chromatographia, 5:286, 1972.

174. D. H. Desty and A. A. Douglas, Study of New Column Forms in Ga Chromatography, J. Chromatog., 158:73, 1978.

175. G. Guiochon and M. F. Gonnord, Fast Analysis of Complex Mixtures Using Narrow-Bore Open Tubular Columns, Paper presented at 1981 American Chemical Society Meeting held in Atlanta, GA, March, 1981.

176. A. S. Said, Peak Capacity and Resolution in Capillary Columns, HRC & CC, 2:637, 1979.

177. N. J. Neu and R. Zinburg, Are We Using the Full Resolving Power of Capillary GC?, HRC & CC, 2:395, 1979.

178. R. E. Kaiser, Working Range of Packed Columns and Capillary Columns in Gas Chromatography, HRC & CC, 1:321, 1978.

179. L. Sojak, J. Krupcik, and J. Janak, Comparison of Capillary Columns Coated with C_{87} Hydrocarbon and Squalane in the Analysis of n-Pentadecane Isomers, J. Chromatog., 191:199, 1980.

180. C. P. M. Schutjes, E. A. Vermeer, J. A. Rijks, and C. A. Cramers, High Speed Profiling of Complex Mixtures by Means of Gas Chromatography in Narrow Bore Capillary Columns, In: Proceedings of Fourth International Symposium on Capillary Chromatography, Hindelang, German, May, 1981.

181. C. P. M. Schutjes, E. A. Vermeer, J. A. Rijks, and C. A. Cramers, Increased Speed of Analysis in Isothermal and Temperature-Programmed Capillary Gas Chromatography by Reduction of the Column Inner Diameter, J. Chromatog., 253:1, 1982.

182. In: Gas Chromatography, N. Brenner, J. E. Callen, and M. D. Weiss, eds., Academic Press, New York, NY, 1962.

183. G. Gaspar, G. Vidal-Madjar, and G. Guiochon, Fast Analysis by Gas Chromatography, Chromatographia, 15:125, 1982.

184. J. Purcell and R. P. W. Scott, Capillary Column Design for High Speed Gas Chromatographic Separation, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

185. D. H. Smith, High-Performance Electrometer Systems for Gas Chromatography, In: Advances in Chromatography, Volume 12, J. C. Giddings and R. A. Keller, eds., Marcel Dekker, New York, NY, 1975.

186. R. J. Jonker, Hans Poppe, and J. F. K. Huber, Improvement of Speed of Separation in Packed Column Gas Chromatography, Anal. Chem., 54:2447, 1982.

187. H. G. Nowicki, C. A. Kieda, and A. S. Nakagawa, Mid-Column Breakage of Commercial Fused Silica Wall Coated Open Tubular Columns Contained in Metal Cage, HRC & CC, 4:236, 1981.

188. G. Schomburg, Future Developments in the Hardware for GC Applications, J. Chromatog. Sci., 21:97, 1983.

189. K. Grob, Elastic Fittings for Glass Capillary Columns, HRC & CC, 1:103, 1978.

190. J. E. Purcell, H. D. Downs, and L. S. Ettre, Extraneous Peaks in Gas Chromatography: Their Source and Elimination, Chromatographia, 8:605, 1975.

191. K. Grob and G. Grob, Capillary Columns with Immobilized Stationary Phases, Part 5: Determination of Column Bleeding; Re-Silylation, HRC & CC, 5:349, 1982.

192. M. W. Redmond and R. D. Condon, Oven Designs for Gas Chromatography: A Realistic Approach, Gas Chromatography Applications, No. GC-AP-010, Perkin-Elmer Corp., Norwalk, CN, 1967.

193. S. G. Hurt and B. Welton, New Microprocessor-Controlled Gas Chromatographs, Amer. Lab., 15(3) 89, 1983.

194. H. U. Buser, R. Soder, and H. M. Widmer, Influence of a Sophisticated Cold Trap on the Shape of Capillary Chromatographic Peaks, HRC & CC, 5:156, 1982.

195. S. Adam, Efficiency of Cryogenic On-Column and Pre-column Focusing of Volatile Compounds for High-Resolution GC, HRC & CC, 6:36, 1983.

196. R. Rothchild and P. R. DeForest, Simple Device for On-Column Cryofocusing in Capillary Column Gas Chromatography, HRC & CC, 5:321, 1982.

197. B. J. Hopkins and V. Pretorious, Rapid Evaporization of Condensed Gas Chromatographic Fractions, J. Chromatog., 158: 465, 1978.

198. J. A. Settlage and W. G. Jennings, Inexpensive Method for Rapid Heating of Cold Traps, HRC & CC, 3:146, 1980.

199. L. R. Hogge and D. J. H. Olson, New Methodology for GC-MS Clarifies Compound Identity, Industrial Research and Development, May, 1982, p. 144.

200. N. Sellier and G. Guiochon, Influence of GC-MS Coupling on the Performances of a Chromatographic Column, J. Chromatog. Sci., 8:147, 1970.

201. E. Wetzel, T. Kuster, and H. C. Curtius, A Split System Applicable as a Gas Chromatographic-Mass Spectrometric Interface and as Effluent Splitter for Specific Gas Chromatographic Detectors, J. Chromatog., 239:107, 1982.

202. F. Friedli, Fused Silica Capillary GC-MS Coupling: A New, Innovative Approach, HRC & CC, 4:495, 1981.

203. P. F. Varadi and K. Ettre, Vacuum Output Gas Chromatography, Anal. Chem., 35:410, 1963.

204. J. F. K. Huber, E. Matisova, and E. Kenndler, Effects of Column Parameters on Optimization of Gas Chromatography-Mass Spectrometry, Anal. Chem., 54:1297, 1982.

205. P. A. Leclercq, G. J. Scherpenzeel, E. A. Vermeer, and C. A. Cramers, Increased Speed of Analysis in Directly Coupled Gas Chromatography-Mass Spectrometry Systems, Part II: Advantages of Vacuum Outlet Operation of Thick-Film Capillary Columns, J. Chromatog., 241:61, 1982.

206. D. Rosenthal, Theoretical Limitations of Gas Chromatographic-Mass Spectrometric Identification of Multicomponent Mixtures, Anal. Chem., 54:63, 1982.

207. R. H. Shaps and A. Varano, Stop-Flow GC-IR Analysis, Industrial Research and Development, February, 1977, p. 86.

208. V. Rossiter, Capillary GC-FTIR, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

209. S. E. Garlock, S. L. Smith, and G. E. Adams, High Resolution Capillary GC-FTIR, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

210. P. R. Griffiths, The Present State-of-the-Art of GC-FTIR and HPLC-FTIR, Paper presented at the 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

211. V. Rossiter, Recent Developments in GC-IR and GC-FTIR, Amer. Lab., 14(2) 144, 1982.

212. A. Robbat, Jr., R. M. Hoes, and C. M. White, Evaluation of a Thermionic Ionization Detector Operated in a Nitrogen Environment for Analysis of Nitrated Polycyclic Aromatic Hydrocarbons via Gas Chromatography, Paper presented at 1983 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

213. Chemical and Engineering News, August 2, 1982, p. 20.

214. G. C. Stafford, Jr., P. E. Kelley, and D. C. Bradford, Advanced Ion Trap Technology in an Economical Detector for GC, Amer. Lab., 15(6) 51, 1983.

215. V. Maynard and E. Grushka, Effect of Dead Volume on Efficiency of a Gas Chromatographic System, Anal. Chem., 44:1427, 1972.

216. W. Blass, K. Riegner, and H. Hulpke, Double-Column Gas Chromatography Using Packed Precolumns and Glass Capillary Main Columns, J. Chromatog., 172:67, 1979.

217. M. Verzele, Capillary or High Resolution Chromatography, HRC & CC, 5:685, 1982.

218. I. M. Hais, Two-Dimensional, J. Chromatog., 187:466, 1980.

219. G. Guiochon, M. F. Gonnord, M. Zakaria, L. A. Beaver, and A. M. Siouffi, Chromatography with a Two-Dimensional Column, Chromatographia, 17:121, 1983.

220. J. Sevcik, Information Content of Multidimensional Switching Systems in Gas Chromatography, In: Advances in Chromatography 1979, A. Zlatkis, ed., University of Houston, Houston, TX, 1979.

221. W. Jennings, A Note on Recycle Chromatography, HRC & CC, 3:86, 1980.

222. L. R. Snyder, J. W. Dolan, and S. Van Der Wal, Boxcar Chromatography: A New Approach to Increased Analysis Rate and Very Large Column Plate Numbers, J. Chromatog., 203:3, 1981.

223. S. R. Lipsky and W. J. McMurray, Recent Developments in the Field of Glass Capillary Column Gas Chromatography, Paper presented at 1981 American Chemical Society Meeting held in Atlanta, GA, March, 1981.

224. G. Guiochon, L. A. Beaver, M. F. Gonnord, A. M. Siouffi, and M. Zakaria, Theoretical Investigation of the Potentialities of the Use of Multidimensional Columns in Chromatography, J. Chromatog., 255:415, 1983.

225. W. Bertsch, Methods in High Resolution Gas Chromatography: Two-Dimensional Techniques, HRC & CC, 1:85, 1978.

226. R. Miller, Multidimensional Gas Chromatography, In: High Resolution Gas Chromatography, 2nd edition, R. R. Freeman, ed., Hewlett-Packard, 1981.

227. J. Sevcik and T. A. Gerner, Extra-Column Effects in Multidimensional Switching Systems (MDSS)-GC, HRC & CC, 2:436, 1979.

228. T. W. Smuts, K. de Clerk, T. G. du Toit, and T. S. Buys, Retention Time and Effective Separation Factor in Series-Coupled Columns with Different Stationary Phases, HRC & CC, 3:124, 1980.

229. T. S. Buys and T. W. Smuts, A Study of the Effects of Temperature and Pressure on the Retention Time in Series - Coupled Columns under Conditions of Constant Mass Flow Rate, HRC & CC, 4:102, 1981.

230. A. Ducass, M. F. Gonnord, P. Arpino, and G. Guiochon, Simple Techniques for Two-Dimensional Gas Chromatography, J. Chromatog., 148:321, 1978.

231. E. L. Anderson, M. M. Thomason, H. T. Mayfield, and W. Bertsch, Advances in Two-Dimensional GC with Glass Capillary Columns, HRC & CC, 2:335, 1979.

232. G. Schomburg, H. Husmann, and F. Weeke, Aspects of Contemporary Capillary Gas Chromatography with Emphasis on Coupled Systems, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

233. R. E. Kaiser and R. I. Rieder, Polarity Change in Capillary GC by Serial-Column Temperature Optimization (SECAT mode in Capillary GC), HRC & CC, 2:416, 1979.

234. B. Welton, M. Goedert, and T. Lyons, Multidimensional Gas Chromatography, Paper presented at 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

235. G. Schomburg, H. Husmann, and F. Weeke, Aspects of Double-Column Gas Chromatography with Glass Capillaries Involving Intermediate Trapping, J. Chromatog., 112:205, 1975.

236. H. Brotell, G. Rietz, S. Sandqvist, M. Berg, and H. Ehrsson, Two-Dimensional Capillary Gas Chromatography Without Intermediate Trapping: Electron Capture Detector Quantitation of an Amino Alcohol (KABI 2128) in Serum after Trifluoroacetylation, HRC & CC, 5:596, 1982.

237. G. Schomburg, F. Weeke, F. Muller, and M. Oreans, Multidimensional Gas Chromatography (MDC) in Capillary Columns Using Double Oven Instruments and a Newly Designed Coupling Piece for Monitoring Detection After Pre-Separation, Chromatographia, 16:87, 1982.

238. W. A. Spencer and L. B. Rogers, Multitemperature Gas Chromatography Using Isothermal Columns in Series, Chem. Biomed. and Environ. Instrumentation, 11(1) 1, 1981.

239. R. J. Phillips, K. A. Knauss, and R. R. Freeman, Applications of Heart Cutting from Packed to Capillary Columns, HRC & CC, 5:546, 1982.

240. K. Herkner and W. Swoboda, The Application of Multicolumn Capillary Gas Chromatography ("Heart-Cutting") to Shorten Analysis Time, Paper presented at Fourth International Capillary Chromatography Symposium, Hindelang, Germany, May, 1981.

241. D. R. Deans, Use of Heart Cutting in Gas Chromatography: A Review, J. Chromatog., 203:19, 1981.

242. E. L. Anderson and W. Bertsch, Heartcutting with Glass Capillary Columns and Selective Detectors, Paper presented at American Chemical Society Meeting, Chicago, August, 1977.

243. J. F. K. Huber, E. Kenndler, W. Nyiry, and M. Oreans, Evaluation of Multi-Stage Gas Chromatography in Quantitative Chemical Analysis, J. Chromatog., 247:211, 1982.

244. D. W. Wright, K. O. Mahler, T. G. M. Weaver, and E. F. Dawes, A Multidimensional GC Conversion System for Vitreous Silica Capillaries, Paper presented at 1983 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

245. V. G. Berezkin, L. N. Kolomiets, A. A. Korolev, Y. B. Shmidel, and V. P. Chizhkov, Compound Chromatography, J. Chromatog., 191:95, 1980.

246. S. P. Cram, A. C. Brown, III, E. Freitas, R. E. Majors, and E. L. Johnson, A Coupled HPLC/GC System: Instrumentation and Automation, Paper presented at the 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectoscopy.

247. R. E. Majors, E. L. Johnson, S. P. Cram, A. C. Brown, III, and E. Freitas, A Coupled HPLC/GC System: Applications, Paper presented at 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

248. R. E. Majors, Multidimensional High Performance Liquid Chromatography, J. Chromatog. Sci., 18:571, 1980.

249. E. L. Anderson and W. Bertsch, Practical Aspects of Pt/Ir Effluent Splitters for Multidetector GC and Pneumatic Solute Switching, HRC & CC, 1:13, 1978.

250. C. D. Chriswell, Recycle Gas Chromatography: Pressure Switching-An Alternative to Mechanical Valves?, HRC & CC, 5:210, 1982.

251. W. Jennings, J. A. Settlage, and R. J. Miller, Multiple Short Pass Glass Capillary Gas Chromatography, HRC & CC, 2:441, 1979.

252. R. J. Miller, S. D. Stearns, and R. R. Freeman, The Application of Flow Switching Rotary Valves in Two-Dimensional High Resolution Gas Chromatography, HRC & CC, 2:55, 1979.

253. G. H. Stewart, Retention Hysteresis in Backflush, J. Chromatog. Sci., 19:216, 1981.

254. R. Annino and J. Leone, The Use of Coanda Wall Attachment Fluidic Switches as Gas Chromatographic Valves, J. Chromatog. Sci., 20:19, 1982.

255. M. Sherenian, R. J. Wolf, Jr., and W. V. Hoef, Chip Mass Flowmeter for Gas Chromatography, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

256. W. Dosch, Unit Construction System for Coupling Operations in High Resolution Gas Chromatography, In: Proceedings of Fourth International Symposium on Capillary Chromatography, Hindelang, Germany, May, 1981.

257. J. Roeraade, Are High Resolution GC Techniques Fully Reliable for Ultra Trace Analysis?, HRC & CC, 1:135, 1978.

258. B. Welton, Column Switching and Backflush Techniques with Open Tubular and Packed Columns in Gas Chromatography, Paper presented at 1978 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

259. H. J. Stan and D. Mrowetz, Residue Analysis of Organophosphorus Pesticides in Food with Two-Dimensional Gas Chromatography Using Capillary Columns and Flame Photometric Detection, HRC & CC, 6:255, 1983.

260. J. S. Warner and R. P. Kenan, Analytical Techniques for Aromatic Components in Aircraft Fuels, Report AFAPL-TR-79-2093, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, OH, October, 1979.

261. F. R. Guenther, S. N. Chesler, and R. M. Parris, The Quantitative Analysis of Some n-Heterocyclics in Shale Oil by Two Dimensional $(GC)^2$, Paper presented at 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

262. J. Sevcik, Determination of Alcohols in Gasoline Blends Using a Multidimensional Switching System, HRC & CC, 3:166, 1980.

263. J. Sevcik, Application of Multidimensional Switching to the Analysis of Volatiles, HRC & CC, 4:86, 1981.

264. J. K. Haken and D. Srisukh, Elimination of the Reference Stationary Phase in Classification Schemes Using the Molecular Retention Index, J. Chromatog., 199:199, 1980.

265. J. Krupcik, J. Mocak, A. Simova, J. Garaj, and G. Guiochon, Optimization of Experimental Conditions for the Analysis of Complex Mixtures by Gas Chromatography, J. Chromatog., 238:1, 1982.

266. M. L. Malczewski and E. Grushka, Multiple Peak Recognition High Performance Liquid Chromatography by Fast Fourier Transformation, J. Chromatog. Sci., 19:187, 1981.

267. M. A. Sharaf and B. R. Kowalski, Quantitative Resolution of Fused Chromatographic Peaks in Gas Chromatography/Mass Spectrometry, Anal. Chem., 54:1291, 1982.

268. B. B. Wheals and J. R. Russell, Electronic Differentiation as an Aid for the Comparison of Size-Exclusion Chromatograms, J. Chromatog., 126:418, 1979.

269. L. M. Linnett and D. J. Atkinson, Electronic Signal Differentiation as an Aid to Quantitation in Gas Chromatography, J. Chromatog., 197:1, 1980.

270. J. Traveset, V. Such, R. Gonzalo, and E. Gelpi, First and Second Derivative Recording of Thin-Layer Chromatograms: Application to the Assay of Unresolved Compounds, J. Chromatog., 204:51, 1981.

271. P. B. Stockwell and I. Telford, Automatic Data Processing in Chromatography - A Mixed Blessing, Chromatographia, 13:665, 1980.

272. S. P. Cram, F. J. Yang, and J. Hinshaw, Quantitation and Data Handling in Capillary GC, Paper presented at 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

273. W. J. Hillan, J. J. Brooks, T. G. Duffy, M. T. Wininger, and W. D. Ross, Trace Chemical Analysis Methodology, Report AFWAL-TR-80-4028, Air Force Materials Laboratory, Wright-Patterson Air Force Base, OH, April, 1980.

274. K. Eckschlager and V. Stepanek, Information Theory in Analytical Chemistry, Anal. Chem., 54:1115A, 1982.

275. S. Wold and M. Sjostrom, SIMCA: A Method for Analyzing Chemical Data in Terms of Similarity and Analogy, In: Chemometrics, Theory and Practice, B. R. Kowalski, ed., American Chemical Soc., 1977.

276. S. A. Borman, Math is Cheaper Than Physics, Anal. Chem., 54:1379A, 1982.

277. J. M. Davis and J. C. Giddings, Statistical Theory of Component Overlap in Multicomponent Chromatograms, Anal. Chem., 55:418, 1983.

278. M. E. Parrish, B. W. Good, F. S. Hsu, F. W. Hatch, D. M. Ennis, D. R. Douglas, J. H. Shelton, D. C. Watson, and C. N. Reilley, Computer-Enhanced High-Resolution Gas Chromatography for the Discriminative Analysis of Tobacco Smoke, Anal. Chem., 53:826, 1981.

279. M. Fatscher and J. M. Vergnaud, Graphic Determination of the Retention Time Obtained by Gas Phase Chromatography with a Longitudinal Temperature Gradient (in French), J. Chromatog., 47:297, 1970.

280. R. Rowan, Jr. and E. W. Leach, Calculations in Programmed Temperature Gas Chromatography When Void Volume is Not Negligible - A New Approach, Anal. Chem., 45:1759, 1973.

281. G. Taylor, Dispersion of Soluble Matter in Solvent Flowing Slowly Through a Tube, Proc. Roy. Soc., A 219:186, 1953.

282. J. J. Van Deemter, F. J. Zuiderweg, and A. Klinkenberg, Longitudinal Diffusion and Resistance to Mass Transfer as a Cause of Non-Ideality in Chromatography, Chem. Eng. Sci., 5:271, 1956.

283. S. J. Hawkes, Modernization of the Van Deemter Equation for Chromatographic Zone Dispersion, J. Chem. Edu., 60:393, 1983.

284. S. N. Chesler and S. P. Cram, Iterative Curve Fitting of Chromatographic Peaks, Anal. Chem., 45:1354, 1973.

285. S. D. Mott and E. Grushka, Chromatographic Solute Identification Using Peak Shape Analysis, J. Chromatog., 126:191, 1976.

286. E. B. Wilson, Advanced Calculus, Ginn and Co., Boston, 1912.

287. S. H. Algie, Empirical Approximations to Equations Based on the Error Function, Anal. Chem., 49: 186, 1977.

288. M. Abramowitz and I. A. Stegun, Applied Mathematics Series--55, National Bureau of Standards, Washington, 1964.

289. E. Katz and R. P. W. Scott, Liquid Chromatography System for Fast, Accurate Analysis, J. Chromatog., 253:159, 1982.

290. J. Ruzicka and E. H. Hanson, Flow Injection Analysis, Wiley and Sons, New York, 1981.

291. W. W. Harman and D. W. Lytle, Electrical and Mechanical Networks, McGraw-Hill, New York, 1962.

292. J. B. Reswick and C. K. Taft, Introduction to Dynamic Systems, Prentice-Hall, Englewood Cliffs, New Jersey, 1967.

293. J. E. Freund, Mathematical Statistics, Prentice-Hall, Englewood Cliffs, New Jersey, 1971.

294. G. A. Korn and T. M. Korn, Mathematical Handbook for Scientists and Engineers, McGraw-Hill, New York, 1968.

295. J. C. Giddings, Advances in the Theory of Plate Height in Gas Chromatography, Anal. Chem., 35:439, 1963.

296. A. T. James and A. J. P. Martin, Gas-Liquid Partition Chromatography: A Technique for the Analysis of Volatile Materials, Analyst (London) 77:915, 1952.

297. J. C. Jaeger, An Introduction to the Laplace Transformation with Engineering Applications, Methssen and Co., London, 1961.

298. H. Cramer, Mathematical Methods of Statistics, Princeton University Press, Princeton, NJ, 1946.

299. E. D. Rainville, Intermediate Differential Equations, 2nd ed., Macmillan, New York, 1964.

300. K. Grob, Twenty Years of Glass Capillary Columns - An Empirical Model for Their Preparation and Properties, HRC & CC, 2:599, 1979.

301. K. Grob, G. Grob, W. Blum, and W. Walther, Preparation of Inert Glass Capillary Columns for Gas Chromatography - A Revised, Comprehensive Description, J. Chromatog., 244:197, 1982.

302. I. Ignatiadis, J. M. Schmitter, and G. Guiochon, Capillary Gas Chromatography of Azaarenes: I. Preparation of Columns, J. Chromatog., 246:23, 1982.

303. J. B. Angell, J. H. Jerman, S. C. Terry, and S. Saadat, A Prototype Gas Analysis System Using a Miniature Gas Chromatograph, Interagency Energy/Environment R&D Program Report, EPA-700/7-80-184, December, 1980.

304. L. S. Ettre, Open Tubular Columns in Gas Chromatography, Plenum Press, New York, 1965, p. 3.

305. W. Bertsch, F. Shunbo, R. Chang, and A. Zlatkis, Preparation of High Resolution Nickel Open Tubular Columns, Chromatographia, 7:128, 1974.

306. D. C. Fenimore, J. H. Whitford, C. M. Davis, and A. Zlatkis, Nickel Gas Chromatographic Columns: An Alternative to Glass for Biological Samples, J. Chromatog., 140:9, 1977.

307. D. C. Fenimore, R. R. Freeman, and P. R. Loy, Determination of Δ^9-Tetrahydrocannabinol in Blood by Electron Capture Gas Chromatography, Anal. Chem., 45:2331, 1973.

308. D. Bombick and J. DiNunzio, Chemically Modified Teflon Wall-Coated Open Tubular Columns for Gas Chromatography, Chromatographia, 14:19, 1981.

309. O. L. Hollis, Gas-Liquid Chromatographic Analysis of Trace-Impurities in Styrene Using Capillary Columns, Anal. Chem., 33:352, 1961.

310. L. Metcalfe and R. Martin, Technique for Coating Gas-Liquid Chromatography Capillary Columns Using Long Chain Quaternary Ammonium Compounds, Anal. Chem., 39:1204, 1967.

311. T. Mon, R. Forrey, and R. Teranishi, Effects of Addition of Absorption-Reducing Material with Open Tubular and Packed Column Gas Chromatography, J. Gas Chromatog., 5:497, 1967.

312. E. Malec, Improved Open Tubular Gas Chromatographic Columns for Use at 250°C and Above, J. Chromatog. Sci., 9:318, 1971.

313. J. Bouche and M. Verzele, A Static Coating Procedure for Glass Capillary Columns, J. Gas Chromatog., 6:501, 1968.

314. E. Ilkova and E. Mistryukov, A Simple Versatile Method for Coating of Glass Capillary Columns, J. Chromatog. Sci., 9:569, 1971.

315. T. Boogaerts, M. Verstappe, and M. Verzele, Experiments with Static and Dynamic Coating Procedures for Glass Capillary Columns, J. Chromatog. Sci., 10:217, 1972.

316. I. Harrison, Freeze-Dry Method for Coating Capillary Columns, Anal. Chem., 47:1211, 1975.

317. G. Dijkstra and J. DeGoey, Use of Coated Capillaries as Columns for Gas Chromatography, In: Gas Chromatography 1958, D. H. Desty, ed., Butterworths, London, 1958.

318. M. Novotny, L. Blomberg, and K. Bartle, Some Factors Affecting the Coating of Open Tubular Columns for Gas Chromatography, J. Chromatog. Sci., 8:390, 1970.

319. M. Novotny and K. Bartle, Preparation of Thick-Film Glass Capillary Columns by the Dynamic Coating Procedure, J. Chromatog., 93:405, 1974.

320. K. Bartle, Film Thickness of Dynamically Coated Open-Tubular Glass Columns for Gas Chromatography, Anal. Chem., 45:1831, 1973.

321. K. L. Ogan, C. Reese, and R. P. W. Scott, Strong, Flexible Soft-Glass Capillary Columns: A Practical Alternative to Fused Silica, J. Chromatog. Sci., 20:425, 1982.

322. P. Sandra, M. Verstappe, and M. Verzele, Whisker Surfaces in $(GC)^2$, HRC & CC, 1:28, 1978.

323. T. I. Wishousky, R. L. Grob, and A. G. Zacchei, Investigation of Whisker-Walled Open Tubular Columns Coated with Manganese (II) Chloride and Cobalt (II) Chloride, J. Chromatog., 249:1, 1982.

324. T. I. Wishousky, R. L. Grob, and A. G. Zacchei, Precautions in Preparing Whisker-Walled Open Tubular Columns, J. Chromatog., 249:155, 1982.

325. T. I. Wishousky, R. L. Grob, and A. G. Zacchei, Deactivation of Whisker-Walled Open Tubular Columns with Octamethyl-cyclotetrasiloxane, J. Chromatog., 249:163, 1982.

326. J. F. G. Clarke, Jr., A Problem in Etching Pyrex Glass Capillary Columns, HRC & CC, 2:357, 1979.

327. M. Verzele, Surface Modification in Glass Capillary Gas Chromatography, HRC & CC, 2:647, 1979.

328. W. E. Dirkes, Jr., A Study of Surface Roughening and Deactivation Techniques for Glass Open Tubular Gas Chromatographic Columns, University of Dayton Research Institute Technical Report, UDR-TR-79-02, January, 1979.

329. W. E. Dirkes, Jr., The Effects of 1,1-Difluoroethane on the Adsorptivity of Glass Capillary Tubing, University of Dayton Research Institute Data Report, UDR-DR-79-07, May, 1979.

330. T. L. Peters, T. J. Nestrick, and L. L. Lamparski, Etching Borosilicate Glass Capillary Columns, Anal. Chem., 54:2397, 1982.

331. A. Venema, J. T. Sukkel, and N. Kampstra, Dynamic Leaching of Sodium-Glass Capillary Columns, HRC & CC, 6:236, 1983.

332. K. Grob, G. Grob, and K. Grob, Jr., Deactivation of Glass Capillary Columns by Silylation, Part 1: Principles and Basic Techniques, HRC & CC, 2:31, 1979.

333. K. Grob, G. Grob, and K. Grob, Jr., Deactivation of Glass Capillaries by Persilylation, Part 2: Practical Recommendations, HRC & CC, 2:677, 1979.

334. G. Schomburg, H. Husmann, and H. Borwitzky, Alkylpolysiloxane Glass Capillary Columns Combining High Temperature Stability of the Stationary Liquid and Deactivation of the Surface, Thermal Treatment of Dealkalinized Glass Surfaces by the Stationary Liquid Itself, Chromatographia, 12:651, 1979.

335. H. T. Badings and J. G. Wassink, Deactivation of Glass Capillary Columns by Dynamic Vapour-Phase Silylation, HRC & CC, 3:21, 1980.

336. R. F. Arrendale, R. F. Severson, and O. T. Chortyk, Preparation of Wall-Coated Open Tubular Glass (Pyrex) Capillary Columns with Polar Stationary Phases, Using Superox®-4 as a Surface Pretreating and Deactivating Agent, J. Chromatog., 208:209, 1981.

337. K. Grob and G. Grob, Static Coating: An Attempt to Optimize a Straightforward Technique Involving Mechanical Closure of the Column, HRC & CC, 5:119, 1982.

338. K. Grob, Static Coating of Glass Capillary Columns, Solvent Selections; Column Filling; Solvent Evaporation, HRC & CC, 1:93, 1978.

339. G. Schomburg and H. Husmann, Methods and Techniques of Gas Chromatography with Glass Capillary Columns, Chromatographia, 8:517, 1975.

340. T. Czajkowska, Parameters Affecting the Quality of Glass Capillary Columns Prepared by the Mercury Plug Dynamic Coating Method, Chromatographia, 15:305, 1982.

341. K. Grob, G. Grob, and K. Grob, Jr., Capillary Columns with Immobilized Stationary Phases, 1. A New Simple Preparative Procedure, J. Chromatog., 211:243, 1981.

342. K. Grob and G. Grob, Capillary Columns with Immobilized Stationary Phases, Part 3: The Basic Influence of Vinyl Groups, HRC & CC, 4:491, 1981.

343. L. Blomberg, J. Buijten, K. Markides, and T. Wannman, Peroxide-Initiated In Situ Curing of Some Silicone Gums for Capillary Columns, HRC & CC, 4:578, 1981.

344. L. Blomberg, K. Markides, and T. Wannman, Glass Capillary Columns for Gas Chromatography Coated with Non-Extractable Films of Cyanosilicone Rubbers, J. Chromatog., 203:217, 1981.

345. M. L. Lee, B. E. Richter, B. A. Jones, J. C. Kuei, S. J. Crowley, and J. S. Bradshaw, Crosslinkable Polar Stationary Phases for Capillary Gas Chromatography, Paper presented at American Chemical Society meeting held in Washington, DC, August, 1983.

346. W. Bertsch, V. Pretorius, M. Pearce, J. C. Thompson, and N. G. Schnautz, An Improved Method for the Preparation of Immobilized Stationary Phases Using Radiation Induced Polymerization, HRC & CC, 5:432, 1982.

347. K. Grob and G. Grob, Capillary Columns with Immobilized Stationary Phases, Part 5: Determination of Column Bleeding; Re-silylation, HRC & CC, 5:349, 1982.

348. L. Blomberg, J. Buijten, K. Markides, and T. Wannman, Peroxide-Initiated in Situ Curing of Silicone Gums for Capillary Column Gas Chromatography, J. Chromatog., 239:51, 1982.

349. M. K. Cueman and R. B. Hurley, Jr., Quick Setting Plug for Capillary Column Making , HRC & CC, 1:92, 1978.

350. C. H. Lochmuller and J. D. Fisk, A Quick and Clean Technique for Sealing Capillary Columns Using the Static Coating Method, HRC & CC, 4:232, 1981.

351. Y. Takayama, An Easy and Reliable Method for End-Sealing Glass Capillary Columns, HRC & CC, 4:533, 1981.

352. T. L. Peters, T. J. Nestrick, and L. L. Lamparski, Sealing Technique for Static Coating of Large Bore Capillary Columns, HRC & CC, 4:588, 1981.

353. K. R. Kim, L. Ghaoui, and A. Zlatkis, Capillary End-Sealing for Static Coating, HRC & CC, 5:571, 1982.

354. C. Spagone and R. Fanelli, Rapid Sealing of Glass Capillary Columns for Static Coating, HRC & CC, 5:572, 1982.

355. W. G. Jennings, Comparison of Fused Silica and Other Glass Columns in Gas Chromatography, Huthig Verlag, Heidelberg, Germany, 1981.

356. H. Saito, High-Purity Fused Silica Capillary Columns for Gas Chromatography, J. Chromatog., 243:189, 1982.

357. W. Jennings, Evolution and Application of the Fused Silica Column, HRC & CC, 3:601, 1980.

358. S. R. Lipsky, W. J. McMurray, M. Hernandez, J. E. Purcell, and K. A. Billeb, Fused Silica Glass Capillary Columns for Gas Chromatographic Analyses, J. Chromatog. Sci., 18:1, 1980.

359. J. Roeraade, Cutting of Glass and Fused Silica Capillaries, HRC & CC, 6:140, 1983.

360. V. Pretorius, J. W. DuToit, and J. H. Purnell, Gas Chromatography in Glass and Fused Silica Capillary Columns: Deactivation of the Inner Surface Using Silicon Films, HRC & CC, 4:344, 1981.

361. S. R. Lipsky and W. J. McMurray, Role of Surface Groups in Affecting the Chromatographic Performance of Certain Types of Fused-Silica Glass Capillary Columns, J. Chromatog., 217:3, 1981.

362. A. Calder, Simple Method for Sealing the Ends of Fused Silica Capillary Columns, HRC & CC, 5:324, 1982.

363. R. F. Arrendale, R. F. Severson, and O. T. Chortyk, Preparation of Fused-Silica Polar Stationary Phase Wall-Coated Open Tubular Columns, J. Chromatog., 254:63, 1983.

364. R. C. Kong, M. L. Lee, Y. Tominaga, R. Pratap, M. Iwao, and R. N. Castle, Mesogenic Polysiloxane Stationary Phase for High-Resolution Gas Chromatography of Isomeric Polycyclic Aromatic Compounds, Anal. Chem., 54:1802, 1982.

365. S. R. Lipsky and W. J. McMurray, Performance of Different Types of Cross-Linked Methyl Polysiloxane Stationary Phases on Fused-Silica Glass Capillary Columns, J. Chromatog., 239:61, 1982.

366. P. A. Peaden, B. W. Wright, and M. L. Lee, The Preparation of Non-Extractable Methyl Phenyl Polysiloxane Stationary Phases for Capillary Column Gas Chromatography, Chromatographia, 15:335, 1982.

367. B. W. Wright, P. A. Peaden, M. L. Lee, and T. J. Stark, Free Radical Cross-Linking in the Preparation of Non-Extractable Stationary Phases for Capillary Gas Chromatography, J. Chromatog., 248:17, 1982.

368. P. Sandra, G. Redant, E. Schacht, and M. Verzele, In Situ Cross-Linking of the Stationary Phase in Capillary Columns, Part 1: Introduction and Preparation of Apolar Columns, HRC & CC, 4:411, 1981.

369. M. L. Lee, P. A. Peaden, and B. W. Wright, Non-Extractable Stationary Phases for Capillary Column Chromatography, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

370. T. J. Stark, P. A. Larson, and B. J. Newton, Crosslinked Polysiloxane Phases for WCOT Columns, Paper presented at 1982 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

371. R. G. Jenkins and R. H. Wohleb, The Use of Bonded Phases in Fused Silica Capillary Gas Chromatography, Paper presented at 1980 Expochem Conference held in Houston, Texas, November, 1980.

372. J. A. Hubball, P. DiMauro, E. F. Barry, and G. E. Chabot, Behavior of Fused Silica Capillaries Subjected to Gamma Radiation, Part 1: Chromatographic Performance, HRC & CC, 6:241, 1983.

373. W. G. Jennings, R. H. Wohleb, and R. G. Jenkins, Factors Affecting Reproducibility in the Manufacture of Glass and Siliceous Glass Open Tubular (Capillary) Columns, Chromatographia, 14:484, 1981.

374. R. C. Kong, and M. L. Lee, Static Coating of Small Diameter Capillary Columns at Elevated Temperatures, HRC & CC, 6:319, 1983.

ABBREVIATIONS AND SYMBOLS

ABBEREVIATIONS

AFS	-- Amperes full scale
ECD	-- electron capture detector
EMG	-- exponentially modified Gaussian
FS	-- full scale
FTIR	-- Fourier transform infrared
GC	-- gas chromatography
GC-FTIR	-- gas chromatography-Fourier transform infrared
GC-IR	-- gas chromatography-infrared
GC-MS	-- gas chromatography-mass spectrometry
HECD	-- Hall electrocoulometric conductivity detector
HFID	-- hydrogen flame ionization detector
HPLC	-- high performance liquid chromatography
HRGC	-- high resolution gas chromatography
ID	-- inside diameter
ITGC	-- isothermal gas chromatography
JP-4	-- a certain classification of jet fuel
MDGC	-- multidimensional gas chromatography
MS	-- mass spectrometer
OD	-- outside diameter
PID	-- photoionization detector
PN	-- part number
PTGC	-- programmed temperature gas chromatography
TSD	-- thermionic specific detector
RSGC	-- rapid separation gas chromatography
UVD	-- ultraviolet detector
WCOT	-- wall coated open tubular
cm	-- centimeter
erf(x)	-- error function of x
in	-- inches
ℓn	-- natural logarithm
log	-- logarithm
m	-- meters
min	-- minutes
mm	-- millimeters
ms	-- milliseconds
mv	-- millivolts
ng	-- nanograms
ppm	-- parts per million
sec	-- seconds
μs	-- microseconds

SYMBOL

A -- area

A -- constant in Equation A18

A_j -- area of j compound

A_s -- asymmetry

B -- asymmetry term, Figure 16

B_h -- asymmetry term, Figure 16

B_k -- asymmetry term, Figure 16

B_o -- specific permeability

$\overline{BC}$ -- asymmetry term, Figure 16

C -- concentration

C_e -- concentration at exit

C_i -- concentration at input

C_o -- concentration at zero; at crest

C_s -- concentration in sphere

C_z -- concentration at location z

$C_i(t)$ -- input concentration as a function of time

°C -- degree Celsius

D_g -- gaseous diffusion coefficient

D_ℓ -- liquid diffusion coefficient

$\mathfrak{D}$ -- denotes distortion

E -- exponential type profile

F -- asymmetry term, Figure 16

F -- volume flow rate, Equation A18

F_c -- constant volume flow rate

F_h -- asymmetry term, Figure 16

F_k -- asymmetry term, Figure 16

G -- Gaussian profile

$\overline{GI}$ -- asymmetry term, Figure 16

H -- height equivalent to a theoretical plate

$\hat{H}$ -- experimentally determined H

$\frac{H}{2}$ -- asymmetry term, Figure 16

$\frac{H}{10}$ -- asymmetry term, Figure 16

ΔH -- heat of vaporization

$H(t)$ -- a response function

$H(\xi)$ -- a convolution term

$H_v(t)$ -- a Hermite polynomial

I_b^a -- Kovats index

K -- constant of integration

L -- column length

$\mathcal{L}$ -- Laplace transform symbol

N_p -- number of effective theoretical plates

R -- ramp profile; gas constant

R_{ij} -- resolution for i and j compounds

T -- temperature

T_o -- initial temperature

T_R -- retention temperature

V_s -- column dead space

V_s -- volume of sphere

W -- mass flow rate

a_n -- coefficient in Gram-Charlier series

a_o -- zeroth coefficient

c -- asymmetry term, Figure 16

c_1 -- a constant

c_n -- general constant

d_f -- film thickness

d_p -- particle diameter

f_1 -- function one

f_2 -- function two

$f_e(t)$ -- excitation function

$f_n(t)$ -- profile terms

$f_r(t)$ -- response function

$f_\omega(t)$ -- resultant output profile

$f_1(\xi)$ -- a convolution term

$g(t)$ -- a time-delay function

h -- asymmetry term, Figure 16

$h(t)$ -- resultant time-delay description

i -- compound i

j -- compound j

j_m -- j solute in mobile phase

j_s -- j solute in stationary phase

k -- partition ratio

k_j -- partition ratio for j compound

k_m -- reciprocal of mixing chamber time constant

k_n -- time-constant reciprocal

m_o -- zeroth moment

m_1 -- first moment

m_n -- nth statistical moment

$m_{1,g}$ -- first moment for inert compound

$\bar{m}_n$ -- nth central moment

$\bar{m}_{2,j}$ -- second central moment for j compound

n -- moment number

n -- number of theoretical plates

n -- number of things or items

n_j -- theoretical plates for j solute

n_p -- number of theoretical plates

p -- pressure

p_i -- inlet pressure

p_o -- outlet pressure

q -- partition ratio plus one

r -- constant rate of temperature increase; terms

s -- Laplace transform term

t -- time

t_a -- time a

t_b -- time b

t_j -- time j

t_m -- time of mobile phase displacement

t_0 -- time zero

t_r -- retention time

t_s -- t_z divided by t_m

t_z -- time corresponding to z location

$t_{r,i}$ -- retention time of i compound

$t_{r,j}$ -- retention time of j compound

t_α -- time of profile mode

t_β -- time of profile median

t_γ -- time of profile mean

$t_{\gamma,g}$ -- time of inert profile mean

$t_{\gamma,j}$ -- time of j profile mean

u -- macroscopic linear gas velocity

u_i -- inlet velocity

u_o -- outlet velocity

v -- axial fluid velocity

$\bar{v}_o$ -- axial fluid velocity, average outlet

w -- weight of solute

w_e -- weight of solute at exit

w_h -- width of half height

w_i -- weight of solute at input, width of i profile

w_j -- weight of j solute

w_o -- weight of solute at time zero

x -- a Cartesian axis

y -- a Cartesian axis

z -- distance axis along the column

z_c -- distance of centroid along the column

Γ -- asymmetry term, Figure 16

α -- relative retention

γ -- a constant

$\delta(t)$ -- delta function term

$\zeta(s)$ -- Laplace tranform term

$\zeta(t)$ -- distribution profile

η -- fluid viscosity

λ -- a constant

$\lambda(t)$ -- variable in Gram-Charlier series

ξ_n -- values of ξ

π -- usual geometrical constant

ρ -- gas density

σ_t -- time-based standard deviation

σ^2 -- variance

$\sigma_{t,j}$ -- j compound standard deviation

ϕ -- Equation B31

$\psi(t)$ -- Gaussian probability function

SUBSCRIPTS

e -- exit

g -- denotes non-retained species

i -- inlet, input

o -- outlet

s -- sphere

APPENDIX A

CHARACTERIZATION OF SOLUTE ZONE MIGRATION

The axial motion of solute zones and the variations in maximum concentration are important in high-resolution gas chromatography. An understanding of these dynamic conditions is necessary when considering new and different OTC gas chromatography separation and analysis modes. In this appendix solute zone motion is discussed, and behavior of the maximum concentration of a solute zone during isothermal migration is described.

1. SOLUTE ZONE AXIAL MOTION IN ISOTHERMAL AND PROGRAMMED-TEMPERATURE OPEN TUBULAR COLUMNS

In the present forms of narrow-bore OTC gas chromatography, the mobile phase experiences only laminar flow. However, this simplistic characterization of mobile phase flow requires elaboration. It has been correctly stated that in gas-liquid chromatography molecular interactions are continually taking place between the gas, the liquid, and the solid phases. Even so, for these flowpaths the longitudinal motion of the macroscopic mobile phase remains in the fluid domain between molecular flow and turbulent flow, that is, in the laminar flow region.

For the case of an isothermal and uniform gas chromatographic column, the mass flow rate through the column can be described by Darcy's law. Specifically,

$$W = \rho u = \left(-\frac{B_o \rho}{\eta}\right)\frac{\partial p}{\partial z} \quad , \tag{A1}$$

where W is the mass flow rate, ρ is the gas density, u is the macroscopic linear gas velocity, B_o is the specific permeability, η is the fluid viscosity, p is the internal column pressure, and z is the distance from the inlet along the axis of the column. In this case, the entire column length experiences the same isothermal temperature. This includes the extremities of the

column, specifically the injector and detector terminations. The GC column is uniform throughout its length with respect to tubing internal diameter, partition ratio, and cross-sectional properties. Consequently, from Boyle's law for ideal gases, and the knowledge that W is constant along the column length,

$$pu = p_i u_i = p_o u_o \quad , \tag{A2}$$

where the subscripts i and o designate inlet and outlet, respectively. Thus, for an isothermal and uniform GC column with constant inlet and outlet pressures,

$$dz = \left(- \frac{B_o p}{\eta p_o u_o} \right) dp \quad , \tag{A3}$$

and, upon integrating according to

$$\int_o^z dz = - \frac{B_o}{\eta p_o u_o} \int_{p_i}^{p} p \, dp \quad , \tag{A4}$$

it is seen that distance and the various pressures are related as

$$z = \frac{B_o}{2\eta} \left(\frac{p_i^2 - p^2}{p_o u_o} \right) \quad . \tag{A5}$$

This equation can also be written to express the behavior when z equals L, which represents the entire column length. That is,

$$L = \frac{B_o}{2\eta} \left(\frac{p_i^2 - p_o^2}{p_o u_o} \right) \quad . \tag{A6}$$

Combining Equations A5 and A6 permits expressing a zone's position along the column as a ratio of column length; specifically,

$$\frac{z}{L} = \left(\frac{p_i^2 - p^2}{p_i^2 - p_o^2}\right) \quad . \tag{A7}$$

Upon, rewriting Equation A7 as

$$p^2 = p_i^2 - \frac{z}{L}\left(p_i^2 - p_o^2\right) \quad , \tag{A8}$$

and since

$$\frac{p}{p_o} = \left(\frac{u}{u_o}\right)^{-1} \quad , \tag{A9}$$

then relative values of column pressure and linear gas-phase velocity can be expressed respectively as

$$\frac{p}{p_o} = \left[p_i^2 - \frac{z}{L}\left(p_i^2 - p_o^2\right)\right]^{\frac{1}{2}} \quad , \tag{A10}$$

and

$$\frac{u}{u_o} = \left[p_i^2 - \frac{z}{L}\left(p_i^2 - p_o^2\right)\right]^{-\frac{1}{2}} \quad . \tag{A11}$$

Profiles of relative pressure and relative velocity versus relative distance are presented in Figures A-1 and A-2. These graphs represent the behavior for inlet-to-outlet pressure ratios of 1.2, 2.0, and 4.0, respectively.

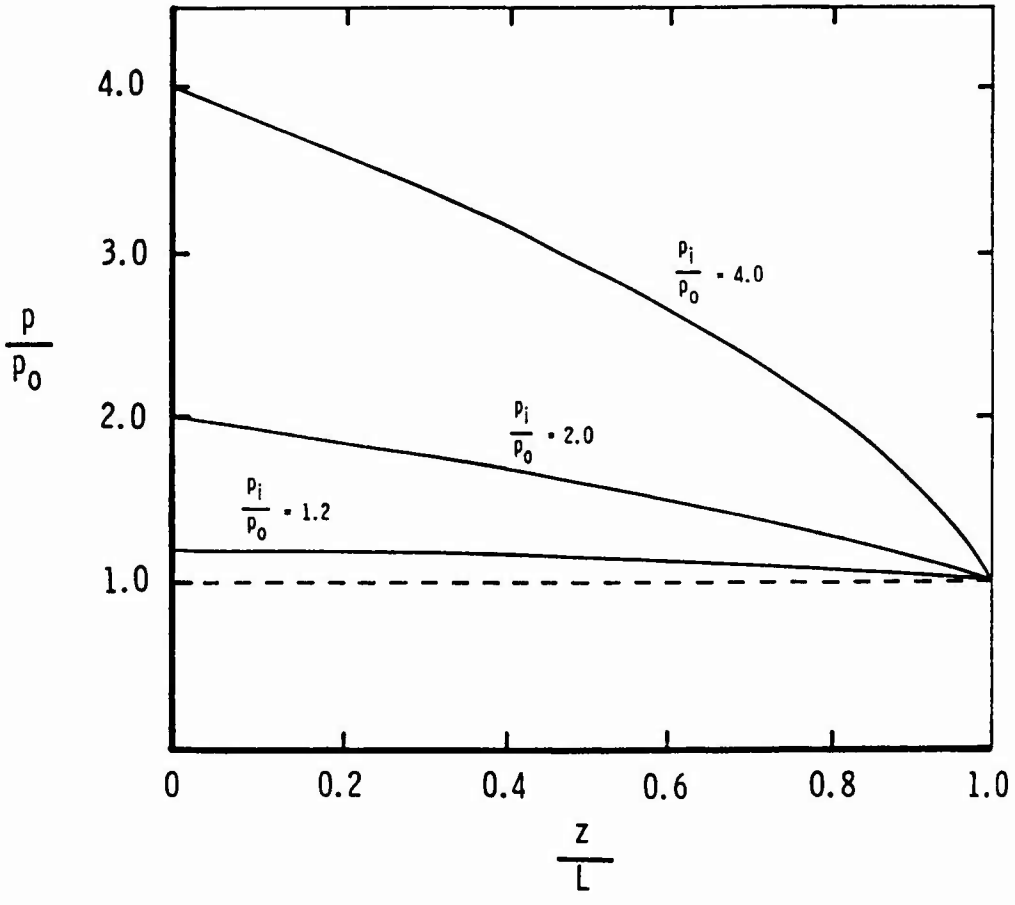


Figure A-1. Graphs of relative pressure versus relative distance.

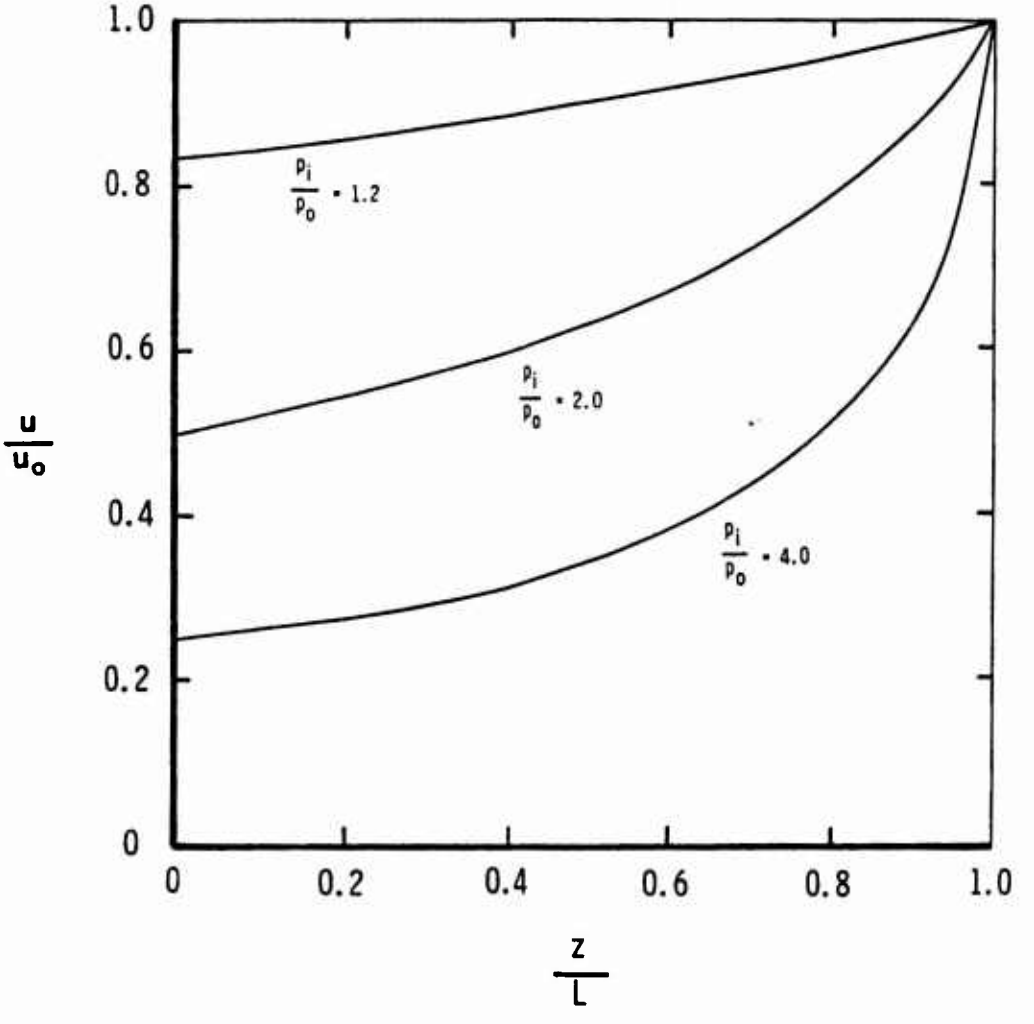


Figure A-2. Graphs of relative velocity versus relative distance.

The time required for the centroid of an unsorbed zone of fluid to flow from the column inlet to a distance z along a homogeneous column can be written as

$$t_z = \int_o^z \frac{dz}{u} = \frac{1}{p_o u_o} \int_o^z \sqrt{p_i^2 - \frac{z}{L}\left(p_i^2 - p_o^2\right)}\, dz \ , \qquad \text{(A12)}$$

and the elapsed time for the mobile phase to traverse the entire column length is

$$t_m = \int_o^{z=L} \frac{dz}{u} = \frac{2}{3}\left(\frac{p_i^3 - 1}{p_i^2 - 1}\right)\frac{L}{u_o} \ ; \quad p_o = 1. \qquad \text{(A13)}$$

Therefore, the migration distance of an unsorbed solute zone can be described implicitly by

$$t_s = \frac{t_z}{t_m} = - \frac{\left[p_i^2 - \frac{z}{L}\left(p_i^2 - 1\right)\right]^{\frac{3}{2}} - p_i^3}{p_i^3 - 1} \ . \qquad \text{(A14)}$$

In the discussion thus far, we have been concerned only with the behavior of isothermal GC columns which are dimensionally uniform throughout their length and subjected only to constant pressure drop conditions. It is assumed that such columns would exhibit constant permeabilities throughout their length. Thus, for this type of column, the time versus distance relationship of an unretained zone can be represented by Equation A12. However, a more useful description of this relationship for both sorbed and unsorbed zones can be written as

$$t_j = \frac{q}{p_o u_o} \int_o^{z=L} \sqrt{p_i^2 - \frac{z}{L}\left(p_i^2 - p_o^2\right)}\, dz \ , \qquad \text{(A15)}$$

where t_j is the elution time of the jth solute zone, k_j is its partition ratio, while

$$q = 1 + k_j \quad , \tag{A16}$$

and, upon integration,

$$t_j = \frac{2Lq}{3p_o u_o} \left[\frac{\left(p_i^3 - p_o^3\right)}{\left(p_i^2 - p_o^2\right)} \right] \quad . \tag{A17}$$

For unsorbed substances the partition ratio is zero. Therefore, it is seen that for unsorbed compounds, Equation A15 is equivalent to Equation A13. For a component zone that experiences a degree of retardation by this type of column, there will be a corresponding q value, specifically, a positive constant greater than unity. Practical values of q usually range between 1.5 and 75.

Programmed temperature gas chromatography (PTGC) is a well established GC mode and is of tremendous value, particularly for analyses of complicated and multicomponent samples with a wide volatility range. There are several different procedures for changing the column temperature in PTGC, such as step increases, continuous and discontinuous programming of temperature, linear and nonlinear temperature versus time profiles, etc. PTGC has several inherently beneficial operational features, not the least of which is its ability to trap and then appropriately release solute zones at the inlet of the column.

There are also numerous techniques for heating selected portions of a column while maintaining other regions at fixed temperatures. In fact, most isothermal gas chromatographic (ITGC) analyses are performed with the injection region (i.e., the inlet portion of the tubing or column) at a higher temperature than the main part of the separation column. Similarly, the outlet region of the column, i.e., that portion attached to the detector inlet assembly, is often at an elevated temperature.

Other techniques reported in the literature describe installations where the temperature varies along the column. The studies by Verguand et al. [279] are of particular interest. These investigators have even studied the dual variation whereby the column oven temperature experiences a programmed increase, while at the same time a substantial thermal gradient exists along the column axis.

The description of the longitudinal motion of zones can be very complicated for these nonisothermal column situations. This complexity can be attributed primarily to the varying thermal circumstances encountered by zones during their passage through the column. One can appreciate the level of this complication by realizing the difficulties in adequately describing the behavior for the most common of the PTGC techniques, specifically, the linear increase of temperature with respect to time. An equation that describes a zone's motion under this PTGC condition [280] is stated as

$$\frac{r}{F} = \int_{T_o}^{T_R} \frac{dT}{A \exp\left(\frac{\Delta H}{RT}\right) + V_s} \quad , \tag{A18}$$

where r is the constant rate of temperature increase, F is volume flow rate per gram of substrate, T is absolute temperature, T_o and T_R are the initial and retention temperatures, respectively. Also, A is a constant related to the entropy of vaporization, ΔH is the heat of vaporization of the solute in the stationary phase, R is the gas constant, and V_s is column dead space. It should be noted that the integral of this particular equation has yet to be solved analytically. One must resort to numerical techniques for this evaluation.

To summarize these examinations of zone motion, it is clear that precise descriptions exist for well-defined ITGC conditions. However, for those situations where a solute zone experiences nonisothermal migration, there are many complexities

associated with accurately describing zone motion, and in view of these, it seems preferable to obtain the flow-dependent qualitative GC data by an isothermal method, when possible.

2. DECLINE IN A SOLUTE ZONE'S MAXIMUM CONCENTRATION DURING ISOTHERMAL MIGRATION THROUGH OPEN TUBULAR COLUMNS

As a solute zone migrates through an isothermal gas chromatographic open tubular column, the zone experiences an increase in axial dispersion. The effect of this dispersion upon maximum solute concentration can be evaluated if every portion of the OTC exhibits a constant plate height, that is,

$$H \equiv \frac{d\left(\sigma_z^2\right)}{dz} = \hat{H} \quad , \tag{A19}$$

where H is the height equivalent to a theoretical plate, σ_z is the distance-based standard deviation of the zone, and $\hat{H}$ is the experimentally determined H. Then, for every point along the column, the variance of the migrating zone will increase directly with distance.* Thus, the standard deviation of the ideally shaped migrating solute zone (a Gaussian profile) can be written as

$$\sigma_z = \sqrt{\hat{H}z} \quad , \tag{A20}$$

while the concentration of such a profile is

$$C_z = \frac{A}{\sigma_z \sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{z - z_c}{\sigma_z}\right)^2\right] \quad , \tag{A21}$$

*In this description, the effects of pressure upon H have been disregarded.

where C_z is the instantaneous solute concentration at a distance z along the column, A is a quantitative factor proportional to the total amount of solute in the zone, and z_c represents the location of the zone centroid along the distance axis.

For a fixed quantity of solute, the maximum concentration of the zone is

$$C_o = \frac{A}{\sigma_z \sqrt{2\pi}} \quad ; \quad z > o \quad , \tag{A22}$$

or, upon the substitution of Equation A20

$$C_o = \frac{A}{\sqrt{2\pi \hat{H} z}} = c_1 z^{-\frac{1}{2}} \quad . \tag{A23}$$

Therefore, Equation A23 describes the maximum solute concentration of a zone as it migrates through the isothermal column.

At any given point in time, the molecules that constitute a retarded solute zone are found in both the stationary phase and the gaseous mobile phase. The distribution between these two isothermal phases is expressed by

$$k_j = \frac{j_s}{j_m} \quad , \tag{A24}$$

where k_j is the partition ratio for the jth solute, and j_m and j_s are the quantities of this solute in the mobile and stationary phases respectively. The previously mentioned A term is directly proportional to the sum of j_m and j_s. Therefore, this A value can be expressed as

$$A = c_2 (j_m + j_s) \quad , \tag{A25}$$

where c_2 is a proportionality constant. From Equations A24 and A25, A can be written as

$$A = c_2 j_s \left(\frac{1 + k_j}{k_j} \right) \quad . \qquad \text{(A26)}$$

This latter equation permits the ready evaluation of the large j_s values as found with the highly retarded zones.

The importance of Equation A23 should not be overlooked. This simple relationship contains important information from which many implications can be drawn. First, let us examine a typical Gaussian solute zone at some distant point along the column. Figure A-3 depicts such a solute profile. If the maximum concentration of the solute present in the column were to exceed the acceptable solubility limit of the liquid substrate or saturate the gas phase volume, this profile would be distorted and axially broadened to a degree. In short, the molecules of this solute zone would not experience strict random migration. The same undesirable behavior would occur if sizable heats of solution or vaporization were experienced as a result of an excessive maximum concentration of solute.

In Figures A-4 and A-5, zone maximum concentration is described with respect to relative distance along the column axis, where L represents the length of the column. In these two figures, four C_o versus distance relationships are depicted. These profiles represent the C_o values which would be generated by columns exhibiting plate heights of 0.25, 0.5, 1.0, and 2.0 mm values, respectively. One of the first conclusions from viewing these profiles is that the inlet portion of the chromatographic column experiences tremendously large C_o values, particularly with respect to those encountered in the remainder of the isothermal column. It is important to realize that these same declining profiles are also valid (within limits) for an unseparated multicomponent sample. Therefore, these concentration profiles are important and instructive when studying the quantitative acceptance of total solute.

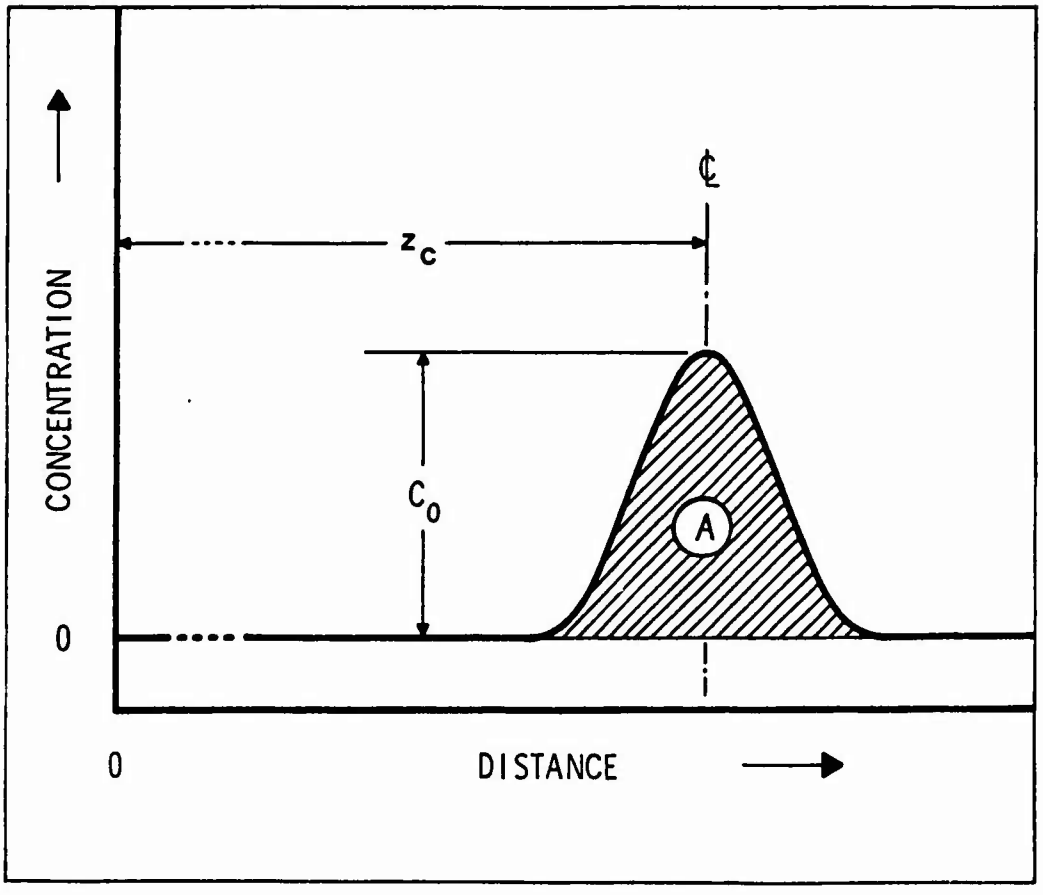


Figure A-3. Typical solute zone.

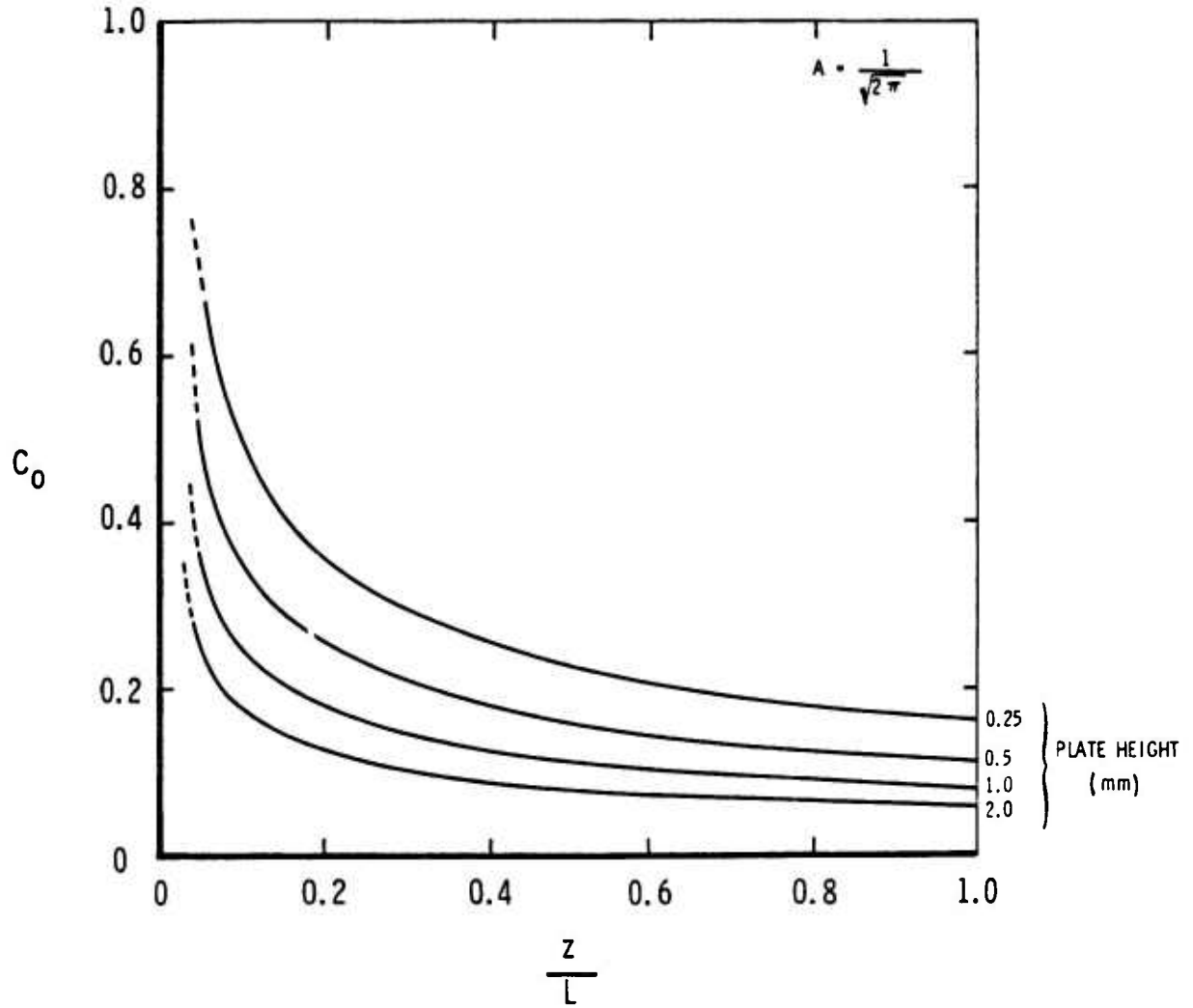


Figure A-4. Variation of maximum concentration of a zone with migration distance.

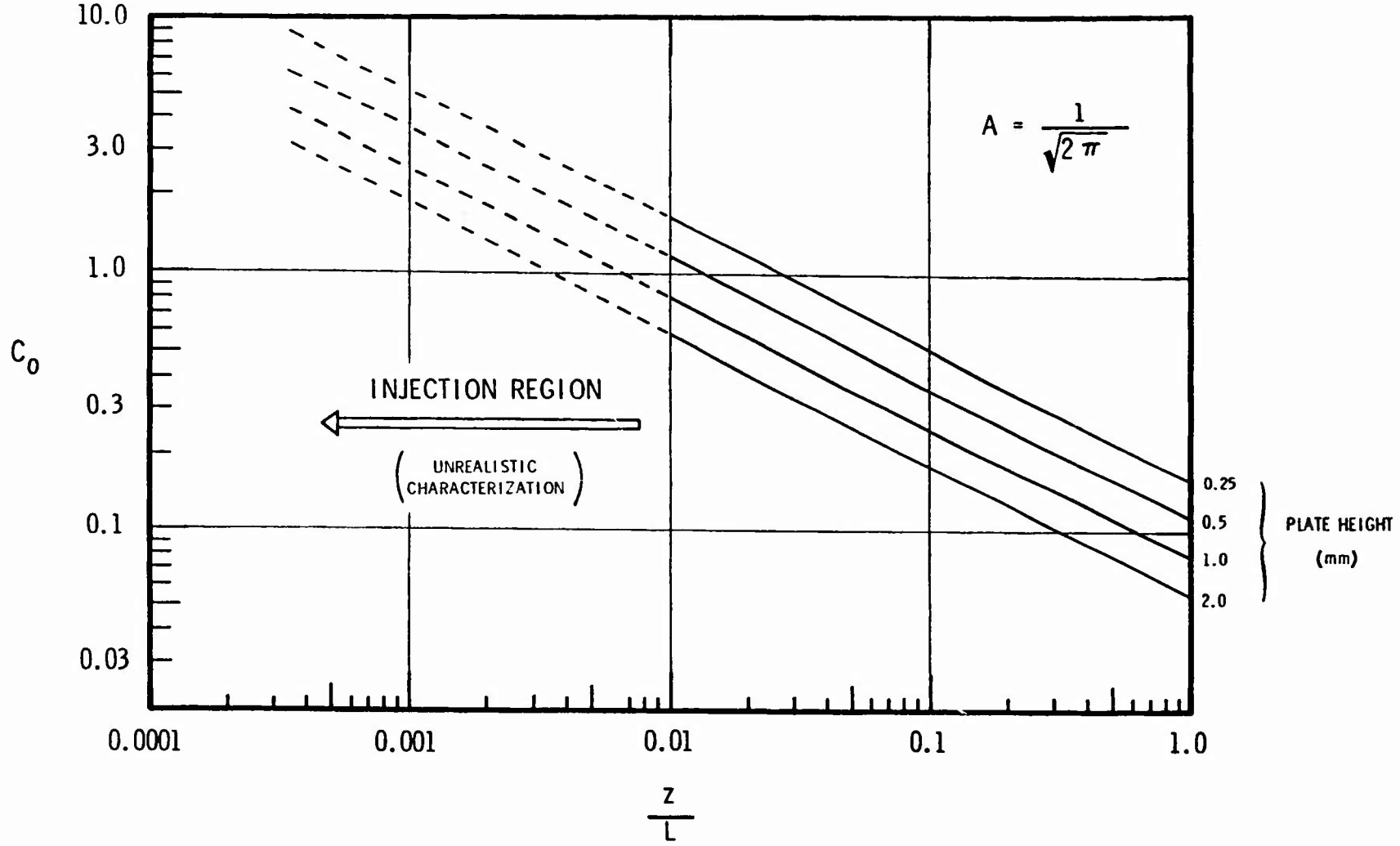


Figure A-5. Log-log representation of C_o versus distance.

This completes the description of the distance-dependent decline in a zone's maximum concentration. During this discussion, simplifying assumptions were made which may not always be realized in normal GC practice. For example, dispersion contributions from the injector portion of the GC instrument can diminish to some extent the large concentrations in the inlet region of the column (see Figure A-5). In addition, some emerging chromatographic zones possess some degree of tailing, i.e., a lagging of solute molecules. As mentioned in the text of this report, this type of asymmetric behavior can be attributed to design aspects of the GC instrumentation system or to adsorptive behavior in the column. Nevertheless, with appropriate design of instrument and column, these undesirable contributions which distort solute zones can be greatly minimized, if not eliminated.

APPENDIX B

CHARACTERISTICS OF RECORDED SOLUTE CONCENTRATION ZONES IN HIGH-RESOLUTION GAS CHROMATOGRAPHY

The concentration profiles of emerging solute zones are of concern in every form of elution chromatography. In HRGC, the shape of the recorded solute concentration zone is especially important, since in many situations it can be the limiting factor with respect to both the chromatographic resolution and the quality of the GC analysis itself.

This appendix addresses five topics in some detail. Although these are separate topics, they are related and, taken as a whole, they provide a basis for examining important characteristics of recorded solute concentration zones relative to HRGC.

1. RESULTANT CONCENTRATION ZONE PROFILES OBTAINED WITH OPEN TUBULAR COLUMN GAS CHROMATOGRAPHIC SYSTEMS

The transport behavior [26,281] of a dilute gaseous zone that is passing through a straight and uncoated (that is, non-retentive) open tube of circular cross section can be described by

$$\frac{\partial C}{\partial t} = - v \frac{\partial C}{\partial z} + D_g \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) , \qquad (B1)$$

where C is the concentration of like molecules in the transport gas, t is time, v represents axial fluid velocity, z is axial distance, D_g is the gaseous intermolecular diffusion coefficient, while x and y represent the mutually perpendicular Cartesian

coordinates. Also, the laminar flow transport of a nonretained solute passing through an open tube that contains significant axial curvature has been described [21].

The dispersion of solute zones as they migrate through gas chromatographic columns has been studied in depth. VanDeemter's early equation [282], which has seen several revisions [283], depicted the dispersion of a migrating solute zone in a packed GC column as

$$H = 2\lambda d_p + \frac{2\gamma D_g}{v} + \frac{8}{\pi^2}\left[\frac{k}{(1+k)^2}\right]\frac{v d_f^2}{D_\ell}, \qquad \text{(B2)}$$

where H is the height equivalent to a theoretical plate, λ and γ are constants, d_p is particle diameter, k is the partition ratio, π is the usual geometrical constant relating the circumference of a circle to its diameter, d_f is liquid film thickness, and D_ℓ is the liquid phase intermolecular diffusion coefficient.

For open tubular gas chromatographic columns, Golay's fundamental equation for such behavior [26] is expressed as

$$H = \frac{2D_g}{\bar{v}} + \frac{1 + 6k + 11k^2}{24(1 + k)^2}\left(\frac{r^2\bar{v}}{D_g}\right) + \frac{2\bar{v}kd_f^2}{3D_\ell(1 + k)^2}, \qquad \text{(B3)}$$

where r is the radius of the gas flowpath and $\bar{v}$ is average linear gas velocity.

Chromatographic zone dispersion has been studied extensively and these descriptions (especially Equation B3) have been shown to be accurate for well-behaved pure solutes that are migrated through lengthy gas flowpaths. However, none of the above descriptions takes into account any form of adsorptive behavior.

For most organic compounds that can be handled by gas chromatography, it is possible to prepare highly efficient OTCs that exhibit a minimum of adsorptive behavior. Even so, every attempt should be made to eliminate even minuscule amounts of adsorptive behavior in HRGC columns.

When an asymmetric elution profile has been generated by a HRGC system, the question arises as to whether the asymmetric behavior was due to adsorption, possibly irreversible adsorption, or whether the profile distortion can be attributed to some other disturbance such as a dead volume which contributes to the skewing of the profile but does not, in effect, limit the quantitative transport of solute molecules through the system. In the former case, quantitative accuracy may suffer when low concentrations of the solute are passed through the system. In the latter case, there is simply a deficiency in the system that should be rectified so that the HRGC system can function at its highest possible performance. As progress and advancements are made in the ultra-high resolution realm of GC, the identification, characterization, and combination of these system deficiencies and time-delay contributors becomes extremely important as they can be the major factors that limit performance.

If intracolumn adsorption can be eliminated, and a sufficiently dilute solute has been properly introduced and transported through a HRGC column, then the emerging concentration zone can be closely approximated by a Gaussian model, written here as

$$\psi(t) = \frac{1}{\sqrt{2\pi}\,\sigma_t} \exp\left[\frac{-(t-t_\gamma)^2}{2\sigma_t^2}\right], \qquad \text{(B4)}$$

where σ_t^2 is the profile's time-based variance, and t_γ is the centroid emergence time of the symmetrical concentration zone. However, if a certain amount of adsorptive behavior is present within the gas chromatographic separation column, then a rather complicated connecting term that contains many vague and ill-defined variables is required for describing the emerging profile.

This connecting term presents several difficulties, as it is concentration dependent and would also vary with different modes of operation, e.g., the temperature versus time relationship in PTGC. Even so, such a connecting function has been hypothesized [284] and studied [285]. One particular function used is a hyperbolic tangent function, and it has been included in descriptions of elution profiles for situations where there is a small amount of adsorptive behavior occurring within the gas-liquid partitioning column.

One particularly troublesome type of recorded solute zone distortion is not amenable to linear system description techniques. This type of distortion occurs when only a fraction of the molecules that have emerged from the ideal HRGC column are subjected to selective adsorptivity within the detection device (see Figure B-1). In short, only a set fraction of the randomly dispersed emerging solute zone is subjected to this distortion. The remaining portion of the molecules (i.e., those following the adsorption-free flowpath) would be sensed without being subjected to this distortion source. Consequently, this is one form of nonlinear system behavior, in that there are two separate flowpaths after emergence from the chromatographic column, one that is distortion-free and the other possessing selective adsorptivity. Fortunately, this particular type of tailing phenomenon can often be described provided the ratios of the two flowpaths are known.

One of the major problems associated with residual levels of adsorptivity in a column is that the apex of the eluting profile will shift in time, and the extent of this event displacement is dependent upon many chromatographic variables. Also, the fixed time-width integrated response of a solute zone can vary if adsorptivity is significant, and this is detrimental to HRGC quantitative analysis.

With early gas chromatographic systems, precolumn dead volumes were known to produce large profile distortions, loss of GC resolution, and considerable solute zone tailing. These

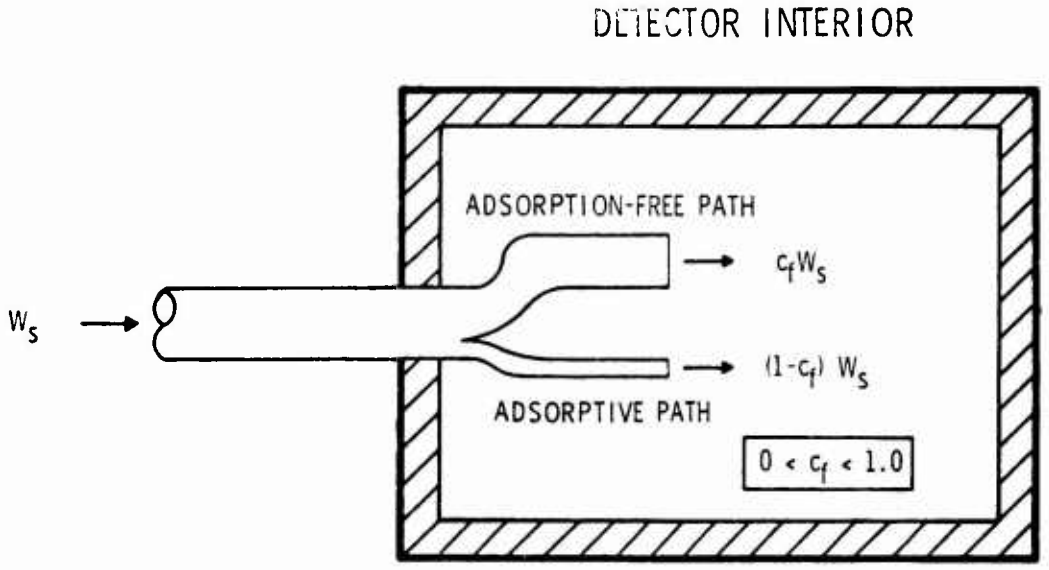


Figure B-1. Behavior of fractionated flows in a faulty effluent device.

precolumn factors were so dominant that post-column dead volumes, unswept recesses, time delays, etc. were largely ignored. This has been especially the case for isothermal gas chromatography where the technique and practice associated with inserting the sample into the chromatographic system are critical. However, with recent dramatically improved sample insertion techniques* that involve special solute focusing procedures, it is now possible to insert complex multi-component samples into a HRGC instrument and expect negligible adverse affects associated with the sample insertion process. Of course, these techniques involve various forms of the programmed temperature mode of HRGC.

For a chromatographic system that contains an adsorption-free HRGC column, along with appropriate sample introduction and intracolumn transport procedures, the characterization of emerging solute zone profiles reduces to the convolution of a Gaussian function (i.e., dispersion produced by unbiased intracolumn zone spreading processes) and an assortment of exponential decay contributions. These delay functions can individually be attributed to:

a) diffusion in unswept recesses,

b) mixing chamber effects,

c) time-lag and dispersion associated with the transport of molecules from the OTC exit to the active region of the detector,

d) surface adsorption phenomena both within transfer lines and upon detector interior components,

e) signal amplification time-constant effects,

f) electrical signal filtration, and

g) subtle time delays associated with the final recording of the amplified output signal.

---

*As seen in Volume II, there are sample insertion procedures that can eventually deposit the sample as a narrow and well-behaved random distribution.

A high-resolution gas chromatograph can be considered and studied as a classical linear system, that is, as a mathematically linear system. Specifically, the separation column and each of the additional individual zone spreading mechanisms (e.g., time delay contributors) can be viewed as acting independently. Therefore, each of these contributions to total recorded zone dispersion is statistically independent.* Once a sample has been properly admitted to an idealized OTC by an appropriate injection process that precedes a programmed temperature gas chromatography procedure, then all subsequent dispersion processes upstream of the column exit can be viewed as random. Also, any time-delay processes occurring downstream of the column exit are essentially of an exponential decaying nature. In short, if the magnitude of the Gaussian function and the details of each of the various independent exponential decay functions are known, then via convolution of the involved contributing terms, i.e., $f_1(t)$ through $f_n(t)$, the resultant output profile, $f_\omega(t)$, can be expressed as

$$f_\omega(t) = f_1(t) * f_2(t) * .... * f_n(t) . \qquad (B5)$$

For every HRGC system there will be finite amounts of profile distortion contributed by each of the many transport, detection, amplification, and signal-recording processes. If, through analysis, contributor isolation, and chromatographic system design, we are able to effectively reduce the exponential decay to a single contributor, this would simplify considerably the profile characterization of effluent zones. For the situation where one of the individual exponential decay terms is dominant to the point that the remaining contributors are negligible, then in this case the single dominant function can

*Surface adsorption associated with certain transport processes may not be statistically independent. However, through appropriate design and selection of materials, this type of nonlinear behavior can be reduced to insignificance.

be convoluted with the column generated Gaussian profile to give a realistic characterization of the recorded output zone distribution. If, however, there are two or more exponential decay functions that are significant, then it is necessary to obtain a resultant profile function that includes each of these exponential decay terms. This case is discussed in Part 4 of this appendix (see page 148). Fortunately, it is usually possible, through available design options, to reduce the attendant residual level of exponential decaying behavior associated with a special HRGC assembly to a single contributor. Then, the single descriptive exponential function that corresponds to this contribution can be convoluted with the Gaussian profile that represents the respective chromatographic column dispersion.

2. DESCRIPTION OF MIXING CHAMBER BEHAVIOR

An individual exponential decay contribution can be examined in a manner analogous to studying the transport behavior associated with a spherical mixing chamber such as shown in Figure B-2. A mass balance for the transport of a solute* through such a mixing chamber can be written as

$$\left(\frac{dw}{dt}\right)_s = \left(\frac{dw}{dt}\right)_i - \left(\frac{dw}{dt}\right)_e , \qquad \text{(B6)}$$

where w is the weight of the solute, and t is time. Subscripts s, i, and e represent the sphere, the input, and the exit, respectively. The solute concentration C within the spherical mixing chamber, of volume V_s, can be expressed as

$$C = \frac{w}{V_s} , \qquad \text{(B7)}$$

*Weight of solute is extremely small compared to the mass of flowing gaseous carrier.

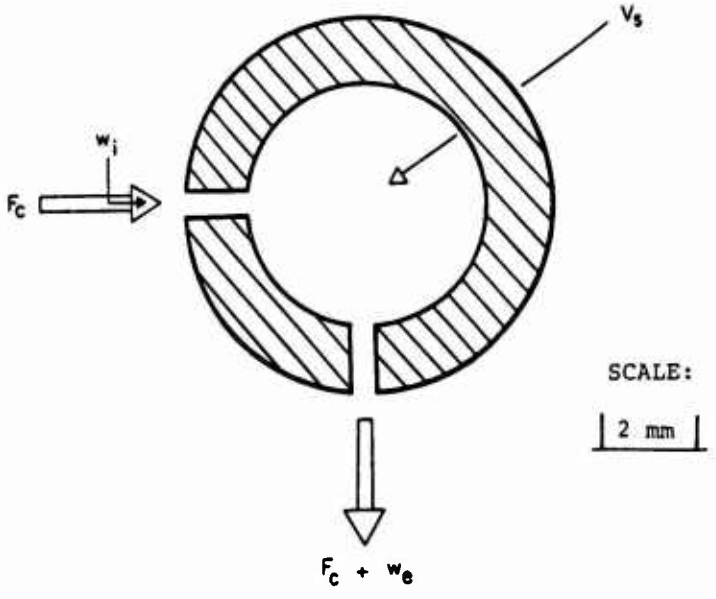


Figure B-2. Cross-sectional view of typical spherical mixing chamber.

and therefore, the constant volume flow rate of carrier gas, F_c, through the chamber is

$$F_c = \frac{V_s}{t} . \tag{B8}$$

Equation B6 can now be rewritten in terms of instantaneous concentrations as

$$V_s\left(\frac{dC}{dt}\right) = F_c(C_i - C_e) , \tag{B9}$$

or

$$\frac{dC}{dt} = \frac{F_c}{V_s}(C_i - C_e) . \tag{B10}$$

Thus, if we assign

$$k_m = \frac{F_c}{V_s} , \tag{B11}$$

where k_m is the reciprocal of the time constant for the mixing chamber, then from Equation B10, the basic differential equation that relates the various concentrations is

$$\frac{dC}{dt} + k_m C_e = k_m C_i , \tag{B12}$$

where both C_e and C_i are functions of time.

Gas-phase equilibration occurs almost instantaneously in a miniaturized mixing chamber (see scale of device shown in Figure B-2). This extremely fast equilibration can be attributed to two factors acting in concert, and these are (1) the flow

induced mixing that is associated with fluid flow in a very small spherical chamber (interior surfaces have high curvature), and (2) the very rapid diffusion of hot gases. Therefore, as a result of this rapid gas-phase equilibration, the following assumption can be made:

$$C \equiv C_s = C_e \ . \tag{B13}$$

Thus, Equation B12 can be rewritten simply as

$$\frac{dC}{dt} + k_m C = k_m C_i \ . \tag{B14}$$

For cases where C_i continues to vary as a function of time, and where the assumption expressed by Equation B13 is still valid, the solute effluent concentration can be expressed as

$$C = \exp(-k_m t) \int k_m C_i \exp(k_m t) dt + K \exp(-k_m t) \ , \tag{B15}$$

and this relationship applies regardless of the functional form of $C_i(t)$. However, when C_i is zero, as is the case immediately following the application of a Diriac delta input pulse, that is,

$$\left.\begin{aligned} \delta(t-t_o) &= 0 \ , \quad t \neq t_o \\ \int_{t_a}^{t_b} \delta(t-t_o)dt &= 1 \ , \quad t_a \leqslant t_o \leqslant t_b \end{aligned}\right\} \ , \tag{B16}$$

then we see that the expression for effluent concentration, i.e., Equation B15 reduces to

$$C = K \exp(-k_m t) \quad , \tag{B17}$$

and since at this same equilibrated initial condition

$$C = \left.\frac{w_o}{V_s}\right]_{t=o} = C_o \quad , \tag{B18}$$

we can then write

$$C = C_o \exp(-k_m t) \quad . \tag{B19}$$

This equation is readily recognized as the same fundamental equation often encountered in chemical reaction studies (i.e., the Arrhenius equation) and in work with electrical circuits (e.g., the behavior of a series resistance--capacitance network). However, of far more importance is the cognizance that Equation B19 also describes the residence time distribution for those gaseous solute molecules which entered the particular spherical mixing chamber under time-invariant or fixed-flow conditions. Expanding on this point, it is important to recognize that the output response resulting from a unit impulse (or more precisely a delta function input, Equation B16) applied to an individual system member describes the residence time distribution contributed by that particular system member. This can be expressed mathematically as

$$\delta(t) * H(t) = \int_{-\infty}^{\infty} H(\xi)\delta(t-\xi)d\xi = H(t) \quad , \tag{B20}$$

where H(t) is a time-based response function.

3. OUTPUT RESPONSE FOR A SINGLE EXPONENTIAL DECAY CONTRIBUTOR AND AN IDEALIZED HIGH-RESOLUTION GAS CHROMATOGRAPHIC COLUMN

As stated earlier, the impulse response for a miniaturized spherical mixing chamber was found to be

$$f_1(t) = c_1 \exp(-k_m t) , \qquad t \geqslant 0 , \tag{B21}$$

and indeed this is the response that would be obtained from a Diriac delta function input. This response function can be normalized by setting

$$c_1 = k_m , \tag{B22}$$

and then

$$f_1(t) = k_m \exp(-k_m t) , \qquad t \geqslant 0 , \tag{B23}$$

If, however, the input pulse was in the form of a normalized Gaussian function (e.g., Equation B4) written here as

$$f_2(t) = \frac{1}{\sqrt{2\pi}\,\sigma_t} \exp\left[- \frac{(t-t_\gamma)^2}{2\sigma_t^2} \right] , \tag{B24}$$

then, the basic expression relating these convolved functions would be

$$h(t) = \int_{\xi_b}^{\xi_a} f_1(\xi) f_2(t-\xi)\, d\xi , \tag{B25}$$

In view of the commutative property of the convolution integral, that is,

$$f_1(t) * f_2(t) \equiv f_2(t) * f_1(t) , \tag{B26}$$

it is also possible to express h(t) as

$$h(t) = \int_{\xi_d}^{\xi_c} f_2(\xi) f_1(t-\xi) d\xi , \tag{B27}$$

where now

$$f_1(t-\xi) = k_m \exp\left[-k_m(t-\xi)\right] , \tag{B28}$$

and

$$f_2(\xi) = \frac{1}{\sqrt{2\pi}\,\sigma_t} \exp\left[-\frac{(\xi-t_\gamma)^2}{2\sigma_t^2}\right] . \tag{B29}$$

Thus, the basic convolution integral for these combined profiles is

$$h(t) = \frac{k_m}{\sqrt{2\pi}\,\sigma_t} \int_{\xi_d}^{\xi_c} \exp\left[-\frac{(\xi-t_\gamma)^2}{2\sigma_t^2}\right] \exp\left[-k_m(t-\xi)\right] d\xi . \tag{B30}$$

If we now let

$$\phi = \frac{\xi - t_\gamma - k_m\sigma_t^2}{\sqrt{2}\,\sigma_t} , \tag{B31}$$

then

$$\frac{d\phi}{d\xi} = \frac{1}{\sqrt{2}\,\sigma_t} , \tag{B32}$$

and

$$d\xi = \sqrt{2}\,\sigma_t\, d\phi \ . \tag{B33}$$

Also, from Equation B31 we can write

$$\xi = \sigma_t\sqrt{2}\,\phi + t_\gamma + k_m\sigma_t^2 \ , \tag{B34}$$

and upon rearrangement and substitution, Equation B30 can be rewritten as

$$h(t) = \frac{k_m}{\sqrt{\pi}} \int_{-\infty}^{\frac{t - t_\gamma - k_m\sigma_t^2}{\sqrt{2}\,\sigma_t}} \exp\left[-\phi^2 + \frac{k_m^2\sigma_t^2}{2} + k_m t_\gamma - k_m t\right] d\phi, \tag{B35}$$

$$h(t) = \frac{k_m}{\sqrt{\pi}} \exp\left[\frac{(k_m\sigma_t)^2}{2} - k_m(t-t_\gamma)\right] \int_{-\infty}^{\frac{t - t_\gamma - k_m\sigma_t^2}{\sqrt{2}\,\sigma_t}} \exp(-\phi^2)\, d\phi, \tag{B36}$$

It has been shown [286] that

$$\int_0^\infty \exp(-t^2)\,dt \equiv \frac{\sqrt{\pi}}{2}. \tag{B37}$$

Therefore, as the error function, erf(x), is defined as

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2)\,dt \ , \tag{B38}$$

and as

$$\frac{2}{\sqrt{\pi}} \int_{-\infty}^{x} \exp(-t^2)dt = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{o} \exp(-t^2)dt + \frac{2}{\sqrt{\pi}} \int_{o}^{x} \exp(-t^2)dt , \quad \text{(B39)}$$

we can also write

$$\frac{2}{\sqrt{\pi}} \int_{-\infty}^{x} \exp(-t^2)dt = 1 + \text{erf}(x) . \quad \text{(B40)}$$

Thus, by expressing the integral of Equation B36 in terms of the error function, that same equation can be rewritten as follows:

$$h(t) = \frac{k_m}{2} \left\{ 1 + \text{erf}\left[\frac{\left(\frac{t-t_\gamma}{\sigma_t}\right) - k_m\sigma_t}{\sqrt{2}} \right] \right\} \exp\left[\frac{(k_m\sigma_t)^2}{2} - k_m(t - t_\gamma) \right] . \quad \text{(B41)}$$

Recently, a very useful semi-empirical equation [287] was introduced which closely approximates the error function. Specifically, this error function approximation,

$$\left.\begin{aligned} 1 + \text{erf}(x) &\cong \frac{(2|x|^2) - 1}{2\sqrt{\pi}\ |x|^3 \exp|x|^2} ; \quad x \leqslant -4 \\ \text{erf}(x) &\cong 1 - 2\left[\exp\left(\frac{K_n x}{|x| + K_d} \right) + 1 \right]^{-1} ; \quad -4 < x < 6 \\ \text{erf}(x) &\cong 1 - \frac{\exp(-x^2)}{x\sqrt{\pi}} ; \quad x > 6 \end{aligned}\right\} , \quad \text{(B42)}$$

where

$$x = \frac{\left(\frac{t-t_\gamma}{\sigma_t}\right) - k_m\sigma_t}{\sqrt{2}} , \quad \text{(B43)}$$

exhibits especially good agreement over a broad application range when $K_n = -15$ and $K_d = -7$. In practical cases, Equation 42 can be used, thus avoiding the necessity of mathematical tables [288] and interpolation for obtaining solutions involving error functions.

By incorporating the Equation B42 empirical error function expressions, Equation B41 can be rewritten as

$$h(t) = \frac{k_m}{2}\left[1 + \text{erf}(x)\right] \exp\left[\frac{(k_m\sigma_t)^2}{2} - k_m(t - t_\gamma)\right] . \quad \text{(B44)}$$

Thus, Equation B44 represents the output response* where a single exponential decay contribution is acting upon the effluent from an idealized HRGC column.

For a linear system which contains just one exponential decay contributor, the following differential equation will apply:

$$\frac{d\left[f_r(t)\right]}{dt} + k_n\left[f_r(t) - f_e(t)\right] = 0, \quad \text{(B45)}$$

where $f_r(t)$ is the response function or signal output, k_n is the reciprocal of the time-constant for the exponential decaying contribution, and $f_e(t)$ is the input, which theoretically can be any real excitation function. From Equation B45 it is apparent that the crests and cols of the response function will occur when

$$\frac{d\left[f_r(t)\right]}{dt} = 0 \; ; \quad 0 < t < \infty . \quad \text{(B46)}$$

Therefore, for input functions that have a single maxima, it is seen from Equation B45 and B46, that

$$f_r(t) = f_e(t) . \quad \text{(B47)}$$

Thus, the crest value of the output response (i.e., the convoluted resultant) will fall on the trailing portion of the input function.

---

*It can be shown from the above equation that profile area does not change with the various independent time constants. However, time of crest occurrence, zone variance, profile maximum height, and elution profile are dependent upon skewing factors.

Again, this descriptive condition applies only for a linear system that incorporates a single exponential decay contributor, and will not be applicable if more than one such contributor is present within the system.

4. CONVOLUTION OF TWO OR MORE INDEPENDENT EXPONENTIAL DECAY CONTRIBUTIONS

The response profile for a single miniaturized mixing chamber has been described in the previous discussion. Attention is now focused upon the resultant behavior of two separate exponential decay contributors which act in series and possess negligible differences in internal pressure. In this particular case, these time-delay functions exhibit different decay time constants.

Let the two separate time-delay functions be described by the following equations

$$f(t) = c_1 \exp(-k_1 t) , \qquad t \geq 0 , \tag{B48}$$

$$g(t) = c_2 \exp(-k_2 t) , \qquad t \geq 0 , \tag{B49}$$

where f(t) represents the isolated first contribution, g(t) is the corresponding profile for the second contribution, c_n is a constant related to the initial effects of a given contribution, and k_n is the reciprocal of the time constant for the particular delay process (subscripts 1 and 2 denote the respective time delay contributor). These two functions can be convolved to obtain the resultant time-delay description h(t), expressed here as

$$h(t) = f(t) * g(t) , \tag{B50}$$

or, stated in terms of the convolution integral

$$h(t) = \int_{-\infty}^{\infty} f(\xi)g(t-\xi)d\xi \ . \qquad \text{(B51)}$$

Therefore, from Equations B48 and B49,

$$c_1 \exp(-k_1 t) * c_2 \exp(-k_2 t) =$$

$$c_1 c_2 \int_{-\infty}^{\infty} \exp(-k_1 \xi) \exp\left[-k_2 t - (-k_2 \xi)\right] d\xi \ , \qquad \text{(B52)}$$

and by rearranging in terms of positive time

$$c_1 c_2 \exp(-k_2 t) \int_{\xi=o}^{\xi=t} \exp\left[\xi(k_2 - k_1)\right] d\xi =$$

$$\frac{c_1 c_2 \exp(-k_2 t)}{k_2 - k_1} \left[\exp(k_2 t - k_1 t) - 1\right] \ , \qquad \text{(B53)}$$

it is seen that the resultant time-delay function can be expressed as

$$h(t) = \frac{c_1 c_2}{k_2 - k_1} \left[\exp(-k_1 t) - \exp(-k_2 t)\right] \ . \qquad \text{(B54)}$$

The curves and conditions presented in Figure B-3 depict one set of the three different time-delay functions that have now been described. Specifically, Figure B-3a is the response curve corresponding to the first time-delay process. Figure B-3b depicts the response profile associated with the second contribution, and Figure B-3c represents the resultant function, or convolution, of the two previous profiles.

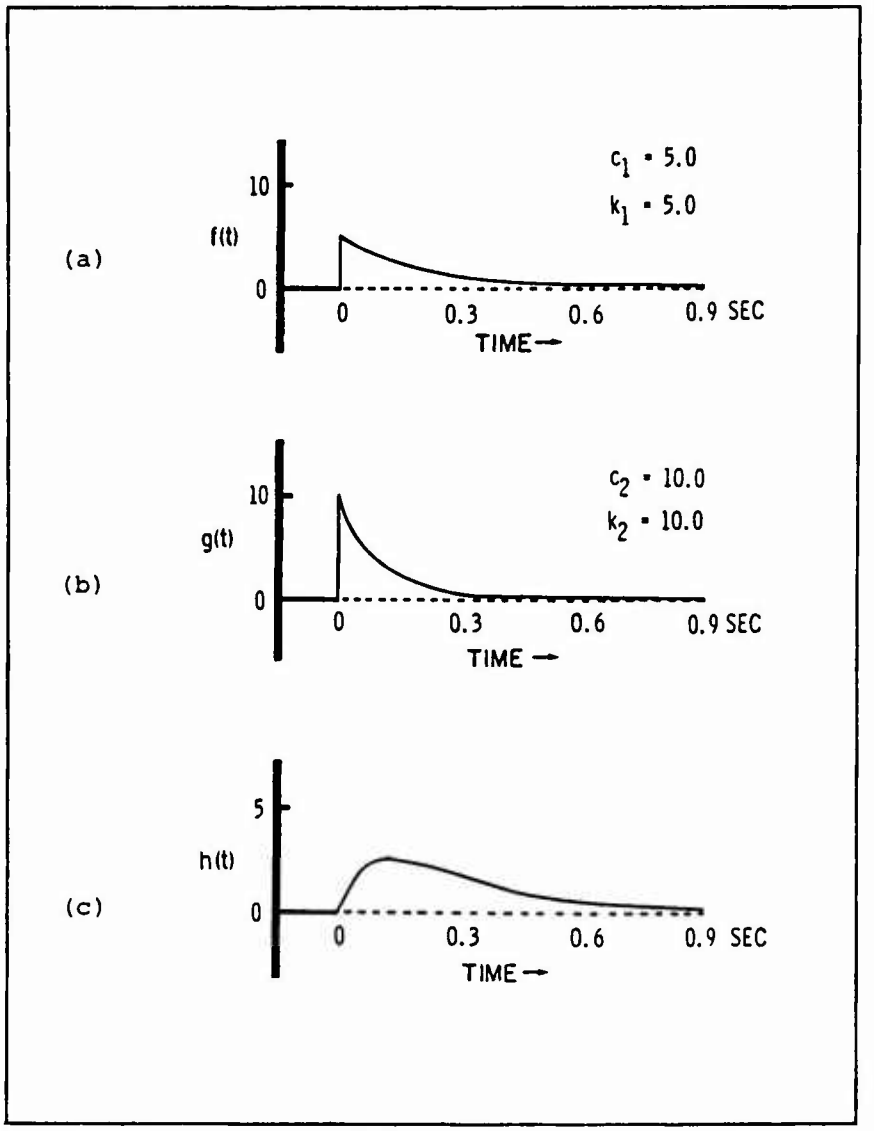


Figure B-3. Three different time-delay functions.

Upon further examination of Equation B54 by setting

$$\frac{d\left[h(t)\right]}{dt} = 0 \ , \tag{B55}$$

we find

$$k_1 \exp(-k_1 t) = k_2 \exp(-k_2 t) \ , \tag{B56}$$

and therefore with the conditions as stated in Figure B-3, h(t) is maximized as shown in Figure B-4 at

$$t = t_\alpha \cong 139 \text{ milliseconds}, \tag{B57}$$

However, the median time, t_β, occurs when

$$\frac{\int_o^{t_\beta} h(t)dt}{\int_o^{\infty} h(t)dt} = \frac{1}{2} \ , \tag{B58}$$

or, in this case when

$$t = t_\beta \cong 246 \text{ ms} \tag{B59}$$

and by evaluating the occurrence in time of the first ordinary statistical moment of this h(t) profile, that is,

$$m_1 = \frac{\int_o^{\infty} t\left[h(t)\right]dt}{\int_o^{\infty} h(t)dt} \ , \tag{B60}$$

we find that the centroid of this skewed or asymmetrical function occurs when

$$t = t_\gamma \equiv m_1 = 300 \text{ ms} \ . \tag{B61}$$

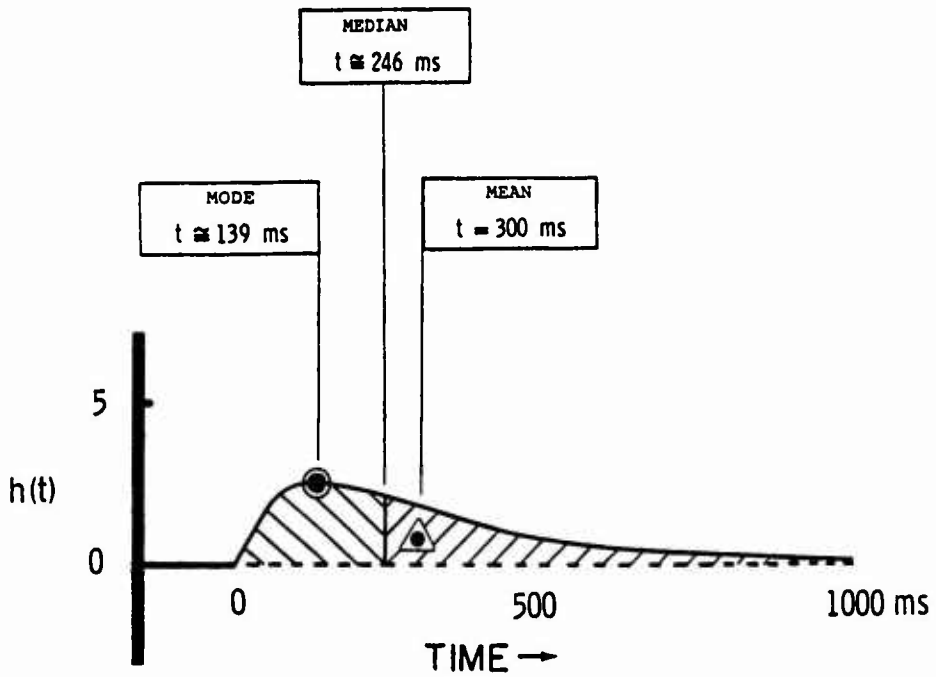


Figure B-4. Statistical characterization of resultant distribution.

As can be seen from Equation B54 and Figures B-3c and B-4, the convolutions of two or more significant exponential decay contributors produce a function with an apex that occurs at a time much greater than zero. Also, the convolution of two or more exponential decay contributors will produce a profile with more extended tailing and a later t_γ occurrence.

Several interesting aspects are revealed upon further analysis of the pair of functions represented by Equations B48 and B49. For example, the maximum resultant time delay will occur when k_1 equals k_2. Conversely, as the difference between k_1 and k_2 increases, it is seen that t_β and t_γ approach the corresponding time values of the exponential decay function described by the smaller k_n value.

The single most important consequence resulting from this particular analysis is that if two or more significant exponential decay terms are present within a Gaussian excited linear process, then the resultant output profile cannot be described by a simple exponentially modified Gaussian (EMG) profile. In general, the distribution resulting from the convolution of a Gaussian term and two or more exponential decay functions will be more delayed in time and more highly skewed. This observation has considerable relevance with respect to advanced work in both high-resolution gas chromatography [175,180,183] and the various modes of rapid separation chromatography [132,186,268,289].

5. CHARACTERIZATION OF EMERGING SOLUTE ZONE PROFILES

For certain multistage linear processes [290-292] including high-resolution gas chromatography [45], it is common to see the individual variances of independent contributors added together and thereby obtain a total variance expression for the overall process. This frequent practice provides only part of the desired information, for even though each contributor is statistically independent, the actual functional distribution of each contribution is of immense importance. Summing each

of the independent variances can indeed obtain the resultant variance for the process [293]; however the shape of the final output profile will not be known unless the individual profiles are also known. During evaluation of the disturbing forces or dispersion associated with a particular linear process this fact is often not taken into consideration. Only in those cases where each of the contributing factors is of a strictly random nature, i.e., a Gaussian distribution, would the system output also be of Gaussian profile. Such a process is rare as some of the individual factors that affect transport behavior and most of the analog signal handling terms are of a time-delay nature, and these are essentially exponential decaying profiles which would, of course, skew a symmetrical input function.

Earlier the characterization of an emerging Gaussian profile was presented, and a Gaussian profile that had been skewed by a single exponential modifying contributor was likewise described. The effects of two individual exponential decaying contributors were also investigated. Furthermore, elution profiles that are composed of a Gaussian major constituent and several other known contributors, some of which may be of an exponential decay nature, can be described using convolution procedures. In addition, these elution profiles can be thoroughly characterized through their statistical moments [294].

For a single modal population distribution, e.g., a pure solute's elution zone profile [63], the ordinary normalized statistical moments can be expressed according to

$$m_n = \frac{\int_{-\infty}^{\infty} t^n[\zeta(t)]dt}{\int_{-\infty}^{\infty} [\zeta(t)]dt} , \qquad \text{(B62)}$$

where $\zeta(t)$ represents the zone profile and n denotes the respective moment. Therefore, it is seen that the first normalized moment would be

$$m_1 = \frac{\int_{-\infty}^{\infty} t[\zeta(t)dt}{m_o} \quad , \tag{B63}$$

where the non-normalized zeroth statistical moment is simply

$$m_o = \int_{-\infty}^{\infty} [\zeta(t)]dt \quad . \tag{B64}$$

Higher statistical moments can also be taken about the mean of the distribution, i.e., the first statistical moment, and these higher order central moments, $\bar{m}_n$, can then be written as

$$\bar{m}_n = \frac{\int_{-\infty}^{\infty} (t - t_\gamma)^n [\zeta(t)]dt}{\int_{-\infty}^{\infty} [\zeta(t)]dt} \quad . \tag{B65}$$

A full knowledge of the statistical moments for a single elution zone would completely characterize the concentration profile. In addition, many of the important chromatographic parameters can be computed directly from measurements of the various statistical moments. For example, the zone profile area, A_j, can be expressed as

$$A_j = m_o = \int_{-\infty}^{\infty} [\zeta(t)]dt \quad , \tag{B66}$$

and the solute zone retention time can be written as

$$t_r = m_1 = \frac{\int_{-\infty}^{\infty} t[\zeta(t)]dt}{A} \quad , \tag{B67}$$

while the profile's time-based profile variance, $(\sigma_t)^2$, can be written as

$$(\sigma_t)^2 = \bar{m}_2 = \frac{\int_{-\infty}^{\infty} (t - t_\gamma)^2 [\zeta(t)]dt}{\int_{-\infty}^{\infty} [\zeta(t)]dt} , \qquad (B68)$$

or, stated in terms of positive time referenced to t equals zero,

$$(\sigma_t)^2 = \bar{m}_2 = \frac{\int_0^{\infty} t^2 [\zeta(t)]dt}{\int_0^{\infty} [\zeta(t)]dt} - \left[\frac{\int_0^{\infty} t[\zeta(t)]dt}{\int_0^{\infty} [\zeta(t)]dt}\right]^2 = m_2 - m_1^2 . \qquad (B69)$$

Profile skewness can be described in terms of the third and lesser statistical moments, while the description of profile excess, degree of kurtosis, or flattening of the population distribution requires definitive information on m_o through $\bar{m}_4$.

After actual measurements of the above statistical moments have been extracted from the chromatographic output data, the height equivalent to a theoretical plate, H, for the respective HRGC arrangement can then be expressed. As by definition [295],

$$H \equiv \frac{d(\sigma_z)^2}{dz} , \qquad (B70)$$

and for low-pressure drop situations where decompression affects [296] can be disregarded

$$H = \frac{(\sigma_t)^2(\bar{v})^2}{L} = \frac{(\sigma_t)^2\left(\frac{L}{t_\gamma}\right)^2}{L} = L\left(\frac{\sigma_t}{t_\gamma}\right)^2 = \frac{(m_2 - m_1^2)L}{m_1^2} = L\,\frac{\bar{m}_2}{m_1^2} . \qquad (B71)$$

Likewise, the total number of theoretical plates, n_p, would be

$$n_p = \left(\frac{t_r}{\sigma_t}\right)^2 = \frac{m_1^2}{\bar{m}_2} \quad , \tag{B72}$$

and the total number of "effective" theoretical plates, N_p, for the jth component can be written as

$$N_p = \left(\frac{t_{\gamma,j} - t_{\gamma,g}}{\sigma_{t,j}}\right)^2 = \frac{(m_{1,j} - m_{1,g})^2}{\bar{m}_{2,j}} \quad , \tag{B73}$$

where the subscript g represents an inert or nonretained species.

These same statistical moments and descriptions of gas chromatographic parameters can also be written in terms of the Laplace transform [297]. For example, the time-based statistical moment function described earlier, i.e., Equation B62, can also be written as

$$m_n = (-1)^n \lim_{s \to 0} \frac{1}{\zeta(s)} \cdot \frac{d^n [\zeta(s)]}{ds^n} \quad , \tag{B74}$$

where

$$\zeta(s) = \int_{-\infty}^{\infty} \exp(-st) \left[\zeta(t)\right] dt = \mathcal{L}\{\zeta(t)\} \quad . \tag{B75}$$

In practice, a recorded solute concentration profile is regarded as a discrete population distribution, and the statistical

moment coefficients and other characterization parameters are then obtained from digitized data. Computation involves counting the average vertical for each electronically filtered standardized increment of the abscissa, computing the specific moment for each of the narrow units (standardized increments) about the central value, appropriate summing and normalization followed by coefficient extraction.

Another method for characterizing the zone profile is by using the Gram-Charlier series [298] which permits a calculation of each of the statistical moments through a rapid conversion expansion involving the Gaussian term, derivatives thereof, and appropriate coefficients related to a series of Hermite polynomials [299]. Certain Hermite polynomials are seen as solutions to the second order differential equation

$$\frac{d^2H}{dt^2} - t\frac{dH}{dt} + nH = 0 \quad , \tag{B76}$$

where n is a nonnegative integer. Specifically, a Hermite polynomial of degree n is defined as

$$H_n(t) = (-1)^n \exp\left(\frac{t^2}{2}\right) \frac{d^n\left[\exp\left(-\frac{t^2}{2}\right)\right]}{dt^n} \quad . \tag{B77}$$

The Gram-Charlier series can be written as

$$\zeta(t) = a_0\lambda(t) + a_3\frac{d^3[\lambda(t)]}{dt^3} + a_4\frac{d^4[\lambda(t)]}{dt^4} + \cdots \quad , \tag{B78}$$

where a_o through a_n are constant expansion coefficients and

$$\lambda(t) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{t^2}{2}\right) \quad , \tag{B79}$$

while

$$a_n = \frac{(-1)^n}{n!}\int_{-\infty}^{\infty} \zeta(t)H_n(t)dt \quad . \tag{B80}$$

Theoretically, if all a_n are known, $\zeta(t)$ is established.

APPENDIX C

FABRICATION TECHNIQUES FOR OPEN TUBULAR GAS CHROMATOGRAPHIC COLUMNS

There are numerous procedures for fabricating and preparing open tubular gas chromatographic columns. Some procedures are simple both in concept and in practice [113] while others are delicate and require extreme attention to detail [300-302]. With the exception of some of the more exotic open-channel gas chromatographic columns, such as a flowpath etched into a silicone wafer [303], the different types of open tubular columns (OTCs) can be classified into three groups. The first group consists of some of the earliest types of OTCs and represents probably the most physically robust columns. This group consists of the various metallic and plastic-walled OTCs. The second group encompasses the many different types of glass OTCs, while the third group comprises the more recently developed fused-silica open tubular chromatographic columns.

1. OPEN TUBULAR COLUMNS PREPARED FROM METAL AND PLASTIC TUBING

The earliest OTC work was conducted using narrow-bore plastic tubing [304] and long lengths of small-bore metal tubing [25]. OTCs have been prepared from Tygon®, Nylon®, and Teflon® plastic tubings. Of these, only Teflon is still being considered as a promising structural material for OTCs. Tygon has definite temperature limitations, plus it exhibits continual leaching of plasticizer. Nylon tubing has an upper-temperature limit of approximately 100°C and also demonstrates significant porosity with respect to water vapor. The various types of organic plastic tubing have limitations with respect to thermal elasticity, and consequently cannot be used at temperatures commonly experienced with metal and glass OTCs.

Several metals have been used for fabricating OTCs. Copper, nickel, gold, and aluminum tubing have been processed into

columns, and a considerable amount of analytical work has used stainless-steel walled OTCs. Several compositions of stainless steel have been used for obtaining high-resolution GC separations of hydrocarbons, and in the 1960's and early 1970's stainless steel was the main tubing material for use in high-resolution gas chromatography. Gold, of course, is a very expensive material with which to construct OTCs, and it has not been used extensively for exactly that reason. Copper has been used extensively; however, it has been demonstrated that this substance presents serious catalytic activities at temperatures above 150°C. Aluminum has been used only in a few instances as it tends to produce an oxide that presents serious adsorption problems. Nickel OTCs have received some attention, as several studies [305-307] have indicated that it can rival stainless steel as a tubing material for OTCs.

The surface microstructure of metal tubing is quite rough, and this is advantageous from a stationary phase wetting standpoint. However, this rough microstructure also tends to present problems with respect to catalytic activity and the production of uneven stationary phase film thicknesses.

Metal capillaries still offer the broadest range of material with respect to available sizes of circular cross-section tubing. Another advantage of metal tubing is that, in most cases, it can be recoated. Also, metal OTCs have excellent thermal properties and tend to even out temperature nonuniformities encountered in oven interiors, at the injector connection and at the column exit.

Once a tubing material has been selected, it is necessary to cleanse the inner wall of processing solvents and other residue. Plastic tubing can generally be readily cleaned with gentle solvents, i.e., those that do not attack the organic polymer. In the case of Teflon, there are studies underway to modify the surface for better adhesion of the stationary phase [308]. The cleaning of new metal tubing can be accomplished through the use of a series of solvents, e.g., pentane, methylene chloride,

acetone, and diethyl ether [309]. Once the metal tubing has been properly cleansed, it can then be subjected to a variety of deactivating procedures whereby surfactants and deactivating agents [310-312] are coated on the surface interior. In some instances, the same surfactants and deactivating agents can be placed in the stationary phase coating solution that will be passed through the narrow-bore tube.

Basically, just two coating procedures are used for preparing plastic or metal-walled gas chromatographic OTCs. The static technique was used by Golay in his original work [25], and it has since been refined by several workers [313-315]. For metal tubes, there is also a freeze-dry static technique which requires the low-temperature evaporation of benzene solvent while under vacuum conditions [316]. Various dynamic processes have also been used for coating both plastic and metal capillaries. Some of these procedures are straightforward [317] while others are highly refined [318-320].

During the preparation of OTCs it is important that dust particles be kept out of the coating solution and also not be admitted to the bore of the narrow tube. Particles tend to accumulate stationary phase which results in adverse performance. Also, small particles may introduce adsorptive sites in the gas chromatographic flowpath. After a column has been properly coated, it should be thermally conditioned in a flowing inert carrier, or conditioned in a static arrangement whereby vacuum and heat are applied simultaneously. Once the column has been thoroughly conditioned and tested, the ends should be sealed and it should be stored at room temperature.

2. BRIEF DESCRIPTION OF TECHNIQUES FOR PREPARING VARIOUS TYPES OF GLASS OPEN TUBULAR COLUMNS

Glass OTCs can be prepared in a wide range of lengths and internal diameters. There are numerous procedures for preparing

these high-performance columns [300,301], and some of these preparation procedures were recently reviewed.

Several different drawing machines can draw conventional glass tubing to an assortment of sizes and lengths. These drawing machines are designed to handle both the Pyrex® glass and the alkali soft-glass tubing. Recently, a technique was developed for drawing flexible soft glass tubing that has a very narrow wall thickness and can be coated with a polymeric outer coating [321]. This type of tubing may have considerable advantage with respect to the ability to coat or bond a range of stationary phases onto the tubing inner surface. Research and development is also continuing in the area of preparing whisker-walled OTCs [27,37,322-325].

New surface treatments and etching methods have been developed for changing the actual surface of a glass that is eventually coated with stationary phase [33,326-331]. Numerous deactivating techniques have also been developed for minimizing adsorptive effects of the glass surface [332-336] and many of these deactivating procedures have been developed for use with the silicone stationary phases which have now been produced in fluid, gum, bonded, or immobilized forms.

The coating procedures for glass tubes have been refined to a high degree and use both the static technique and the mercury plug dynamic process [337-340]. The recently developed immobilized stationary phases for glass OTCs have received considerable attention [341-348] and it appears that these types of phases will be used extensively in the future. Along with these advances, there have been several new procedures [349-354] for sealing the filled tube prior to removing the volatile solvent. These sealing techniques have made it possible to increase the reproducibility of column preparation.

3. SURVEY OF FUSED SILICA OTC PREPARATION PROCEDURES

The availability of high-quality fused silica tubing has permitted the fabrication of high-performance OTCs that are

specially durable [30,31]. Polyimide externally coated fused silica tubing is commercially available with inside diameters ranging from 25 to 400 microns. Also, this unprocessed tubing can be obtained in practically any length up to one kilometer. Larger internal diameters of fused silica tubing are somewhat limited, for as the bore diameter increases, the flexibility of the tubing diminishes considerably. The widest bore fused silica tubes currently available commercially are of approximately 0.4 mm inside diameter.

Open tubular columns which have been fabricated from fused silica tubing exhibit several distinct advantages. The fused silica columns do not require any end straightening and can be placed directly in special injectors or detectors. Also, the inertness of the fused silica surface is a major advantage. In addition, their flexibility and ease of installation are certainly desirable attributes.

Several recent studies have evaluated fused silica open tubular GC columns [355-358] and these evaluations were conducted primarily for assessing the behavior of high-purity fused silica coated tubes with respect to their chromatographic performance using a variety of different chemical samples. The evolution of this type of OTC and its performance when compared to conventional glass capillaries has been investigated at length.

Due to the flexibility of the polyimide protected fused silica tube and its ease of handling, practically any desired length of open tubular section can be readily prepared. However, considerable attention should be given to cutting the coated quartz tubing, as it is important that an even cut be made at both the injector end of the column and at the exit where the OTC would be installed in a high-temperature detector [359]. Once the raw fused silica tubing has been cut to length, it can be deactivated by several processes [360,361]. One of the more common deactivating techniques involves an in-situ pyrolysis of 20 M polyethylene glycol. Another popular procedure consists of pyrolyzing silicone on the fused silica surface and then removing the residue with several solvent flushes. Silicone films and a

variety of other deactivating processes using silylation agents have also been employed with good results.

Fused silica tubing can be coated with stationary phase using the dynamic technique which employs a mercury plug; or they can be filled and subsequently coated using the static technique, as simple methods for sealing the ends of the fused silica capillary have recently been developed [362].

The desirability of producing polar fused silica OTCs has been expressed, and considerable progress has been made in this particular area [363]. There has also been considerable interest in obtaining highly selective liquid crystal stationary phase OTCs, and recently several of these columns were prepared and applied to the separation of polynuclear aromatic hydrocarbons. These particular columns have the very desirable feature of producing dramatically different retention properties at slightly different column temperatures [364].

The application of chemical bonded stationary phases (also referred to as immobilized stationary phases) to fused silica tubing has been a major improvement in OTC technology. As the outer coatings of most fused silica tubes can now withstand approximately 350°C for long periods of time, it is possible to conduct a wide variety of crosslinking processes to liquid phases that have been deposited in these tubes.

There are many advantages to these immobilized stationary phase OTCs. As the stationary phase is nonextractable, it is possible to chemically remove contaminants from these columns by passing potent solvents, such as methylene chloride, through the tubing to wash out or dissolve impurities. In addition, these immobilized stationary phase OTCs have been shown to be usable to very low cryogenic temperatures (-50 to -100°C) and still function as a chromatographic column. Several workers have subjected these phases to liquid nitrogen temperatures without any mechanical failure of the gas flowpath. In short, the polyimide protected tubing maintains its integrity for brief intervals at -196°C.

Research into fabricating techniques for producing bonded phase OTCs is ongoing [365-372] and indeed excellent results are being obtained from numerous procedures for crosslinking and surface attachment of the stationary phase. Some of the most desirable aspects of the bonded phase OTCs are their excellent film stability and the very low phase bleed. With the use of special static coating techniques and the different procedures for preparing bonded phase OTCs, good reproducibility is obtained in the OTC fabricating process [373]. Also, static coating techniques have been developed for coating microbore fused silica OTCs, and these types of columns seem to have a considerable future in some of the special application areas of high-resolution gas chromatography [374].

Fused silica tubing is somewhat limited with respect to surface treatments in that etching cannot be readily accomplished and certainly the growth of whiskers is not permissible with such thin-walled fused silica tubes. However, chemical bonding of very thick stationary phase films (1.0 to 8.0 micron layers) has been accomplished with fused silica tubing.

Chemically bonded fused silica capillary columns are available from a variety of column manufacturers and a wide variety of different size uncoated tubing is also commercially available.

☆U.S. Government Printing Office: 1985 — 559-065/20814